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Zerovalent Palladium and Platinum Complexes Containing Rigid Bidentate Nitrogen Ligands and Alkenes: Synthesis, Characterization, Alkene Rotation and Substitution Reactions. X-ray Crystal Structure of [Bis((2,6-diisopropylphenyl)imino)acenaphthene](maleic anhydride)palladium(0)[1]

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A number of zerovalent palladium and platinum M(NN)(alkene) complexes, containing the rigid bidentate nitrogen ligands bis(arylimino)acenaphthene (Ar-BIAN) and bis(phenylimino)camphane (Ph-BIC) have been synthesized and characterized. Stable complexes were obtained with electron poor alkenes, such as dimethyl fumarate, fumaronitrile, maleic anhydride, and tetracyanoethylene. Complexes bearing asymmetric Ar-BIAN or Ph-BIC ligands occurred as mixtures of isomers. From IR, UV, and ^1H and ^{13}C NMR spectroscopy and from substitution reactions it was concluded that the back-donation of electron density from the metal to the alkene is the major factor determining the stability of the complexes. Some of the complexes show fluxional behavior on the NMR time scale, which was explained by rotation of the alkene around the metal–alkene bond. The estimated rotation barriers of 50–69 kJ/mol for Pd and >72 kJ/mol for Pt are high as compared to reported values for other palladium and platinum alkene complexes. From a study of alkene substitution reactions of Pd(Ar-BIAN)(alkene) complexes it appeared that alkene substitution occurs via a fast associative mechanism for complexes containing Ph-BIAN or *p*-Tol-BIAN ligands and via a slower dissociative mechanism for complexes containing *o,o'-i*-Pr$_2$C$_6$H$_3$-BIAN. Substitution of the *p*-Tol-BIAN ligand in Pd(*p*-Tol-BIAN)(alkene) by *o,o'-i*-Pr$_2$C$_6$H$_3$-BIAN is also observed and is explained by initial dissociation of the alkene. Whereas the spectroscopic and crystal data point to M(II)–metallacyclopropane type structures, the reactivity points rather to M(0)–alkene type complexes. The X-ray crystal structure of Pd(*o,o'-i*-Pr$_2$C$_6$H$_3$-BIAN)(maleic anhydride) has been determined. Crystals are triclinic, space group $P\bar{1}$, with $a = 10.9931(9)$ Å, $b = 11.7313(5)$ Å, $c = 14.7906(13)$ Å, $\alpha = 86.276(5)°$, $\beta = 81.936(7)°$, $\gamma = 71.273(5)°$, $Z = 2$, and final $R = 0.055$ for 3702 reflections with $I > 2.5\sigma(I)$.

Introduction

There has been considerable interest in the chemistry of palladium and platinum complexes containing π-coordinated unsaturated ligands,[2,3] which may, apart from the interesting structure of and bonding in this type of complexes, be ascribed to the fascinating catalytic reactions involving platinum and palladium η²-alkene and η²-alkyne complexes.[3] In most cases, the active species are divalent complexes, and as a consequence

most attention has been directed toward alkene and alkyne complexes with square planar divalent palladium and platinum metal centers. More recently also a number of reports of five-coordinated Pt(II) and Pd(II) alkene complexes in a trigonal bipyramidal environment have appeared.[4-6] The investigations dealing with alkene and alkyne complexes of zerovalent group 10 metals have mainly concentrated on Pt(0) and Ni(0), but Pd(0) complexes have received less attention.

Models, based on the qualitative description by Dewar[7] and Chatt and Duncanson[8] and on theoretical studies,[9] indicate that the metal alkene bond can be described as a combination of σ-donation from a filled alkene π-orbital to an empty metal

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localized orbital and π-back-donation from a filled metal orbital to an empty alkene π*-orbital. In zerovalent palladium and platinum complexes having a d^{10}-configuration, the π-back-donation from the electron rich metal center to the alkene is the most important contribution, as is shown by (i) the low-frequency shift of the alkene protons and carbon atoms in NMR upon coordination, (ii) the observation that upon coordination of electron poor alkenes thermally more stable complexes are obtained,[10] and (iii) the unreactivity of the coordinated alkene toward nucleophilic attack.

In square planar divalent Pd/Pt alkene complexes the contribution of the π-back-donation from the metal to the alkene is usually much smaller than in zerovalent complexes, and electron rich alkenes give the most stable complexes. For five-coordinate trigonal bipyramidal Pd(II) and Pt(II) complexes, however, it has been suggested that the π-donation from the metal center to the alkene is more important in determining the stability of the metal–alkene bond as compared to square planar Pd(II) and Pt(II) complexes.[5d,11] These complexes have a very similar arrangement of the ML₂(alkene) or ML₂(alkyne) moiety as in the trigonal planar zerovalent complexes, as opposed to square planar M(II) complexes.

(M = Pd, Pt)
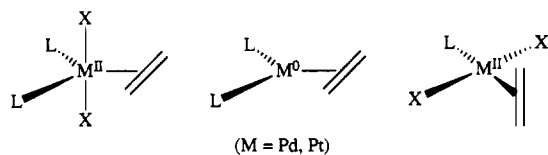
We describe here the synthesis and characterization of zerovalent complexes of palladium and platinum of the type M(NN)(alkene), containing rigid bidentate nitrogen ligands.[12] These palladium complexes are efficient catalysts for homogeneous hydrogenation and carbon–carbon cross-coupling reactions, as described previously.[13] As the zerovalent complexes combine an electron rich d^{10} metal center with an electron-donating nitrogen ligand and an electron-accepting alkene, we investigated the bonding in terms of σ-donation and π-back-donation by variation of the alkene and the bis(nitrogen) ligand. Furthermore the dependency of substitution reactions and alkene rotation on the bis(nitrogen) ligand and the alkene has given valuable information about electronic and steric effects on the stability of the complexes. We were also interested in the synthesis and properties of asymmetric complexes, which can be obtained by choosing the appropriately substituted NN ligands. The results obtained from these studies are of importance for the understanding of the reactivity of the zerovalent complexes toward oxidative addition[14] and their application in catalytic reactions.[13]

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Experimental Section

Pd(Ar-BIAN)(alkene) and Pd(Ph-BIC)(alkene) Complexes (1–9a–d). Pd(Ph-BIAN)(DMFU) (1a). A mixture of 0.58 g of Pd(DBA)₂ (1.0 mmol) or 0.52 g of Pd₂(DBA)₃·CHCl₃ (0.50 mmol), 0.36 g of Ph-BIAN (1.1 mmol), and 0.16 g of DMFU (1.1 mmol) in 40 mL of acetone was stirred overnight at 20 °C. After 16 h the mixture was evaporated to dryness and the solid product washed with diethyl ether (2 × 20 mL). The product was dissolved in dichloromethane (50 mL) and filtered through Celite filter aid to remove metallic palladium. The residue was washed with dichloromethane until the washings were (almost) colorless (4 × 20 mL) and the combined filtrates were evaporated to dryness. The product was washed with diethyl ether (4 × 15 mL) and dried in vacuo, giving 0.41 g of a dark purple to red product (70%).

The other zerovalent palladium complexes were synthesized in a similar way, except the TCNE complexes (1d and 2d) which were formed within 2 h at room temperature. Pd(Ar-BIAN)(DMFU) complexes were dark purple to red, MA and FN complexes red and TCNE complexes orange, whereas Ph-BIC complexes were orange to yellow. Yields were in the range 70–80%. All complexes showed correct analytical data.

Pt(Ar-BIAN)(alkene) and Pt(Ph-BIC)(alkene) Complexes (10–12b–d). Pt(p-Tol-BIAN)(FN) (10b). A mixture of 0.31 g of Pt(DBA)₂ (0.47 mmol), 0.18 g of p-Tol-BIAN (0.50 mmol), and 40 mg of FN (0.51 mmol) in 40 mL of THF was stirred overnight at 45 °C. After 16 h the mixture was evaporated to dryness and the solid product washed with diethyl ether (2 × 10 mL). The product was redissolved in dichloromethane (40 mL) and filtered through Celite filter aid. The residue was washed with dichloromethane until the washings were (almost) colorless (4 × 20 mL) and the combined filtrates evaporated to dryness. The solid was washed with diethyl ether (3 × 15 mL) and dried in vacuo, yielding 0.18 g of a dark purple powder (63%).

Other zerovalent platinum complexes were synthesized in the same way in 60–65% yield. Pt(Ar-BIAN) complexes were dark purple, whereas Ph-BIC complexes were red to orange. The complexes showed correct analytical data. Pt(bpy)(DMFU) has been obtained by this procedure in 65% yield (bpy = 2,2′-bipyridine). ^1H NMR (CDCl₃): 9.22 dt (2 H, $^3J(Pt–H)$ = 30.9 Hz, $^3J(H–H)$ = 5.3 Hz, $^4J(H–H)$ = $^5J(H–H)$ = 1.2 Hz), 8.08 m (2 H), 8.03 m (2 H), 7.47 m (2 H), bpy; 3.75 s (=CH, $^2J(Pt–H)$ = 93.7 Hz), 3.64 s (OMe), DMFU.

Reactions with Dimethyl Butynedioate (DMBD). (A) To a suspension of 116.3 mg of Pd(DBA)₂ (0.20 mmol) (or 104.5 mg of Pd₂(DBA)₃·CHCl₃ (0.10 mmol)) and 70.3 mg of Ph-BIAN (0.21 mmol) in 10 mL of acetone was added 50 μL of DMBD (0.41 mmol) and the mixture stirred at 20 °C. After 1 h the brown suspension was evaporated in vacuo to about 1 mL, and 20 mL of diethyl ether was added to precipitate the product. The product was washed with another 20 mL of diethyl ether and dried in vacuo. Further purification was achieved by dissolution of the product in 30 mL of dichloromethane and filtration over Celite filter aid. The residue was washed with dichloromethane (3 × 10 mL) and the combined filtrates evaporated to dryness. The product was washed with diethyl ether (3 × 10 mL) and dried in vacuo yielding 124 mg (83%) of 13 as an orange-yellow solid. Anal. Found (calcd for C₃₆H₂₈N₂O₈Pd): C, 59.18 (59.80); H, 4.22 (3.90); N, 3.85 (3.87). ^1H NMR (CDCl₃): 6.44 d (7.2 Hz), H₃; 8.00 d (8.2 Hz), H₅; 7.3–7.7 m (12 H),

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Table 1. Crystal Data for Pd(o,o'-i-Pr$_2$C$_6$H$_3$-BIAN)(MA) (5c)

formula	C$_{40}$H$_{42}$N$_2$O$_3$Pd	T, K	300
a, Å	10.9931(9)	λ, Å	0.71073
b, Å	11.7313(5)	space group	$P\bar{1}$
c, Å	14.7906(13)	Z	2
α, deg	86.276(5)	D_x, g cm^{-3}	1.310
β, deg	81.936(7)	μ, cm^{-1}	5.5
γ, deg	71.273(5)	R^a	0.055
V, Å^3	1788.2(4)	$R_w{}^b$	0.048

^{a} $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

H$_4$, H$_{9-13}$; 3.57 s, 2.97 s, O*Me*. ^{13}C NMR (CDCl$_3$): 161.4, C$_1$; 126.2, C$_2$; 126.4, C$_3$; 128.2, C$_4$; 132.0, C$_5$; 131.7, C$_6$; 146.0, C$_7$; 147.1, C$_8$; 122.0, C$_{9,13}$; 130.2, C$_{10,12}$; 129.1, C$_{11}$; 145.8, Pd—*C*=C; 162.9, Pd—C=*C*; 172.5, 171.4, C=O; 51.8, 51.6, CO$_2$*Me*. IR (KBr): 1705, C=O; 1200, C-O; 1649, 1621, C=N. Mass: found m/z = 722 (calcd m/z 722).

(B) To a solution of 58 mg of **1a** (0.099 mmol) in 10 mL of acetone was added 25 μL of DMBD (0.204 mmol) and the mixture stirred at 20 °C. Immediately a light brown suspension appeared, which was evaporated to dryness after 30 min. The product consisted of a mixture of uncoordinated DMFU and the palladacyclopentadiene product **13**, which showed the same spectral data as the product synthesized via method A. Purification of the product was achieved in the same way as described above.

(C) To a solution of 50 mg of **13** (0.069 mmol) in 10 mL of THF was added 17 μL of DMADC (0.139 mmol) and the mixture stirred at 20 °C. After 3 h the solvent was evaporated and the product analyzed by ^{1}H NMR spectroscopy (in CDCl$_3$), indicating the formation of C$_6$(CO$_2$-Me)$_6$ (singlet at 3.88 ppm).

Alkene Exchange and Substitution Reactions. For each reaction a representative example is given. Other reactions were carried out in a similar fashion.

(A) Alkene Exchange. A mixture of 14.3 mg of Pd(o,o'-i-Pr$_2$C$_6$H$_3$-BIAN)(MA) (**5c**) (0.020 mmol) and 2.0 mg of MA (0.020 mmol) was dissolved in 0.50 mL of CDCl$_3$, and an NMR spectrum was recorded.

(B) Alkene Substitution. A mixture of 55.2 mg of Pd(o,o'-i-Pr$_2$C$_6$H$_3$-BIAN)(MA) (**5c**) (0.078 mmol) and 6.1 mg of FN (0.078 mmol) was dissolved in 10 mL of acetone and stirred at 20 °C. After 1 h the solution was evaporated to dryness and the solid washed with diethyl ether (2 × 3 mL) and dried in vacuo. The mixture was analyzed by NMR spectroscopy in CDCl$_3$.

Ligand Substitution Reactions. To a solution of 30.3 mg of Pd(p-Tol-BIAN)(MA) **2c** (0.054 mmol) in 1 mL of CDCl$_3$ was added 26.9 mg of o,o'-i-Pr$_2$C$_6$H$_3$-BIAN (0.054 mmol), and the reaction was monitored by NMR spectroscopy.

X-ray Crystal Structure Determination of Pd(2,6-i-Pr$_2$C$_6$H$_3$-BIAN)-(MA) (5c). Crystals suitable for X-Ray diffraction were obtained by slow evaporation of a solution of Pd(o,o'-i-Pr$_2$C$_6$H$_3$-BIAN)(MA) (**5c**) in dichloromethane/methanol (6:1 v/v). X-ray data were collected on an ENRAF-NONIUS CAD4 diffractometer for an orange-red crystal mounted on top of a glass fiber. Unit cell parameters have been derived from the 25 SET4 setting angles in the range 7 < θ < 12°. A total of 8482 reflections were scanned, corrected for Lp, resulting in 3702 reflections with $I > 2.5\sigma(I)$. The structure was solved with DIRDIF 92[20] and refined on F with SHELX 76.[21] Hydrogen atoms were taken into account at calculated positions and refined riding on their carrier atoms with three common isotropic thermal motion parameters. Convergence was reached at $R = 0.055$ for 3702 observed reflections with $I > 2.5\sigma(I)$. Numerical details have been collected in Table 1. Scattering factors were taken from ref 22, corrected for anomalous dispersion.[23] Calculations were done on a DEC 5000/ULTRIX system. Geometrical data were calculated and the illustration prepared with PLATON.[24] Final coordinates for the non-hydrogen atoms have been compiled in Table 2.

Results

Synthesis of Complexes. Zerovalent palladium complexes containing bis(arylimino)acenaphthene (Ar-BIAN) and 2,3-bis-

Table 2. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for Pd(o,o'-i-Pr$_2$C$_6$H$_3$-BIAN)(MA) (5c)

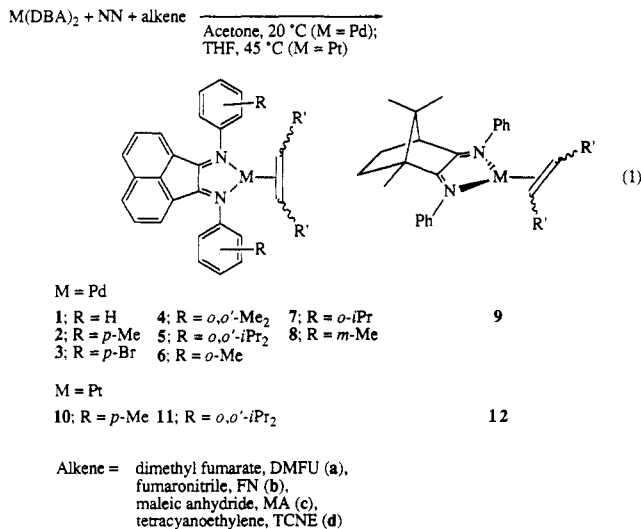| atom	x	y	z	U(eq),^{a} Å^2
Pd(1)	−0.12658(5)	0.79948(5)	0.20653(4)	0.0425(2)
O(1)	0.0824(5)	0.5865(5)	0.3023(4)	0.076(3)
O(2)	0.1753(6)	0.7251(7)	0.3234(5)	0.109(3)
O(3)	−0.0050(5)	0.4690(5)	0.2382(5)	0.096(3)
N(1)	−0.2371(5)	0.9809(4)	0.2502(3)	0.0378(19)
N(2)	−0.3223(5)	0.8016(4)	0.2058(3)	0.0374(17)
C(1)	−0.4076(6)	0.9054(5)	0.2254(4)	0.039(2)
C(2)	−0.5497(6)	0.9527(6)	0.2335(4)	0.043(3)
C(3)	−0.6474(7)	0.9085(6)	0.2237(5)	0.058(3)
C(4)	−0.7749(7)	0.9840(7)	0.2416(6)	0.074(3)
C(5)	−0.8066(7)	1.1003(7)	0.2664(5)	0.063(3)
C(6)	−0.7091(6)	1.1493(6)	0.2777(5)	0.049(3)
C(7)	−0.7263(7)	1.2670(6)	0.3055(5)	0.055(3)
C(8)	−0.6222(7)	1.3015(6)	0.3151(5)	0.059(3)
C(9)	−0.4936(6)	1.2250(5)	0.2986(5)	0.048(3)
C(10)	−0.4741(6)	1.1105(5)	0.2706(4)	0.036(2)
C(11)	−0.5810(6)	1.0731(5)	0.2610(4)	0.038(2)
C(12)	−0.3587(6)	1.0044(5)	0.2491(4)	0.037(2)
C(13)	−0.3679(6)	0.7045(6)	0.1909(5)	0.050(3)
C(14)	−0.4172(7)	0.6463(6)	0.2658(6)	0.063(3)
C(15)	−0.4600(10)	0.5535(8)	0.2465(8)	0.104(5)
C(16)	−0.4580(12)	0.5229(9)	0.1594(10)	0.132(6)
C(17)	−0.4048(11)	0.5765(9)	0.0880(7)	0.110(5)
C(18)	−0.3563(7)	0.6682(6)	0.1009(6)	0.064(3)
C(19)	−0.2974(8)	0.7306(7)	0.0230(5)	0.068(3)
C(20)	−0.2135(10)	0.6446(9)	−0.0505(6)	0.117(5)
C(21)	−0.3982(10)	0.8346(9)	−0.0180(7)	0.123(5)
C(22)	−0.4198(8)	0.6818(7)	0.3618(6)	0.068(3)
C(23)	−0.2905(10)	0.6317(10)	0.3937(7)	0.118(5)
C(24)	−0.5233(10)	0.6497(10)	0.4303(7)	0.127(5)
C(25)	−0.1972(6)	1.0747(5)	0.2816(5)	0.041(3)
C(26)	−0.1615(6)	1.1556(6)	0.2165(5)	0.051(3)
C(27)	−0.1405(7)	1.2539(6)	0.2503(7)	0.065(3)
C(28)	−0.1484(7)	1.2692(7)	0.3405(8)	0.076(4)
C(29)	−0.1727(7)	1.1841(9)	0.4022(6)	0.080(4)
C(30)	−0.1991(7)	1.0841(7)	0.3741(6)	0.059(3)
C(31)	−0.2238(11)	0.9902(10)	0.4431(7)	0.106(5)
C(32)	−0.3409(10)	1.0185(12)	0.5001(9)	0.197(8)
C(33)	−0.1123(11)	0.8992(9)	0.4669(9)	0.155(6)
C(34)	−0.1471(8)	1.1326(7)	0.1152(6)	0.072(3)
C(35)	−0.2615(9)	1.2069(12)	0.0712(7)	0.158(7)
C(36)	−0.0249(8)	1.1477(9)	0.0638(6)	0.110(5)
C(37)	0.0274(7)	0.5583(7)	0.2315(7)	0.068(4)
C(38)	0.0198(7)	0.6490(6)	0.1597(6)	0.060(3)
C(39)	0.0743(7)	0.7321(6)	0.1880(6)	0.058(3)
C(40)	0.1186(8)	0.6895(8)	0.2750(7)	0.076(4)

^{a} U(eq) = one-third of the trace of the orthogonalized U.

(phenylimino)camphane (Ph-BIC), of the general formula Pd-(NN)(alkene), were synthesized in good yield by reaction of Pd(DBA)$_2$ or Pd$_2$(DBA)$_3$·CHCl$_3$ (DBA = dibenzylideneacetone) with the appropriate bis(nitrogen) ligand in the presence of an electronpoor alkene, like dimethylfumarate (DMFU), fumaronitrile (FN), maleic anhydride (MA) or tetracyano ethylene (TCNE) (eq 1). The analytical data confirm the 1:1:1 ratio of the metal, NN ligand, and alkene.

When less electron accepting alkenes (dimethyl maleate, methyl acrylate, acrylonitrile, *trans*-stilbene, styrene, and cyclohexene) were employed no Pd(NN)(alkene) complexes could be isolated. Contrary to the cases for 2,2'-bipyridine and phenanthroline,[17,25] no formation of Pd(Ar-BIAN)(DBA) or Pd(Ph-BIC)(DBA) complexes was observed in these reactions. Attempted synthesis of complexes with dimethyl maleate or methyl acrylate starting from Pd$_3$(TTAA)$_3$ (TTAA = tritoluylideneacetylacetone), a method which gave good results for the synthesis of labile Pd-(DAB)(alkene) complexes (DAB = 1,4-diaza-1,3-butadiene),[10e] did not lead to the desired complexes either. For p-BrC$_6$H$_4$-BIAN, stable Pd(0) complexes have been isolated only with

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(23) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
(24) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

(25) Ito, T.; Takahashi, Y.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1972**, 629.

M(DBA)₂ + NN + alkene ———————————————
Acetone, 20 °C (M = Pd);
THF, 45 °C (M = Pt)

(1)

M = Pd

1; R = H	**4**; R = o,o'-Me₂	**7**; R = o-iPr	**9**
2; R = p-Me	**5**; R = o,o'-iPr₂	**8**; R = m-Me	
3; R = p-Br	**6**; R = o-Me		

M = Pt

10; R = p-Me **11**; R = o,o'-iPr₂ **12**

Alkene = dimethyl fumarate, DMFU (**a**),
fumaronitrile, FN (**b**),
maleic anhydride, MA (**c**),
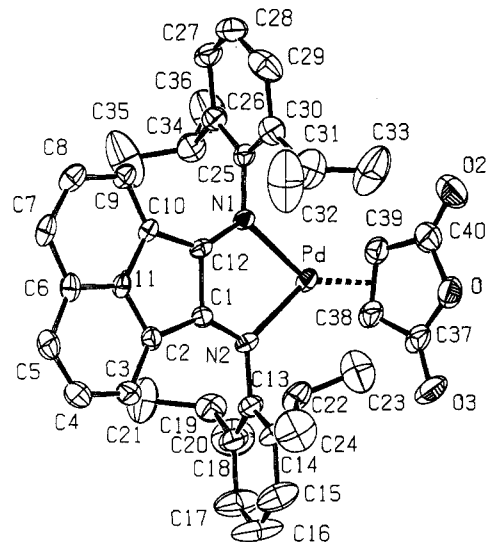tetracyanoethylene, TCNE (**d**)

DMFU and FN (**3a,b**), but not with MA. No oxidative addition of the aromatic bromide occurred during the synthesis of these complexes, and the zerovalent complexes were the only products formed.

Analogous zerovalent platinum complexes Pt(Ar-BIAN)-(alkene) and Pt(Ph-BIC)(alkene) have been synthesized in a manner similar to that used for the palladium complexes. Because of the slower substitution at platinum as compared to palladium, the reactions were best carried out at 45 °C. Electron poor alkenes are again necessary to stabilize the complexes. When FN, MA, and TCNE were employed, stable complexes were obtained in reasonable to good yield, but no stable Pt(Ar-BIAN)(DMFU) and Pt(Ph-BIC)(DMFU) complexes could be isolated. We have, however, synthesized Pt(bpy)(DMFU) by this procedure.

X-ray Crystal Structure of Pd(2,6-i-Pr₂C₆H₃-BIAN)(MA) (5c). The molecular structure and the adopted numbering scheme are presented in Figure 1. Selected bond distances, bond angles, and torsion angles have been compiled in Table 3. The structure shows that the palladium center is coordinated by the N(1), N(2), C(38), and C(39) atoms. The coordination around the palladium center is trigonal planar as expected for zerovalent complexes of the type ML₂(alkene) (M = Pd, Pt).[2c] Comparison with the data of the uncomplexed p-Tol-BIAN[12c] reveals some slight changes in the ligand which must be ascribed to the combined effects of changing the aromatic group on the imine N atoms and coordination to the palladium center. The imine C=N bonds N(1)–C(12) and N(2)–C(1) of 1.276(9) and 1.297(7) Å, respectively, are slightly longer than in the free p-Tol-BIAN (1.267(3) Å). Furthermore, upon coordination, the distance between the imine C atoms C(1)–C(12) has decreased, the distance between the N atoms N(1) and N(2) has decreased, the diimine plane is more planar (the torsion angle N(2)–C(1)–C(12–N(2) is close to 0°), and the aromatic groups on the imine N atom are bent more toward the naphthalene backbone, away from the palladium center. The angle between the planes of the naphthalene and the aromatic N substituents is closer to perpendicular in Pd(o,o'-i-Pr₂C₆H₃-BIAN)(MA) (about 76 and 86°) than in the free ligand (about 61°), but this must be ascribed to the o-isopropyl substituents on the aromatic groups, rather than to the coordination to palladium.

The alkene bond C(38)–C(39) in the complex is 0.105 Å longer than in the free alkene[26] and is comparable to that in Pd-(Me)Cl(9,10-Me₂Phen)(MA)[6a] and Pt(η⁴-1,5-hexadiene)(MA).[27] The other distances in the MA part are very similar in the three complexes and the free molecule. The large angles Pd—C—C(=O) (106.4(6) and 108.7(6)°) are probably caused

(26) Marsh, R. E.; Ubell, E.; Wilcox, H. E. *Acta Crystallogr.* **1962**, *15*, 35.
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Figure 1. ORTEP drawing (30% probability level) of Pd(o,o'-i-Pr₂C₆H₃-BIAN)(MA) (**5c**).

Table 3. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for [Pd(o,o'-i-Pr₂C₆H₃-BIAN)(MA)] (**5c**) (Esd's in Parentheses)

Pd–N(1)	2.173(5)	O(2)–C(40)	1.186(12)	C(1)–C(2)	1.471(10)
Pd–N(2)	2.145(6)	O(3)–C(37)	1.204(10)	C(1)–C(12)	1.506(9)
Pd–C(38)	2.051(7)	N(1)–C(12)	1.276(9)	C(10)–C(12)	1.478(9)
Pd–C(39)	2.077(8)	N(1)–C(25)	1.433(8)	C(37)–C(38)	1.445(12)
O(1)–C(37)	1.387(11)	N(2)–C(1)	1.297(7)	C(38)–C(39)	1.408(11)
O(1)–C(40)	1.408(11)	N(2)–C(13)	1.424(8)	C(39)–C(40)	1.442(13)

N(1)–Pd–N(2)	77.78(19)	C(1)–N(2)–C(13)	117.9(6)
N(1)–Pd–C(39)	124.4(2)	N(2)–C(1)–C(2)	134.5(6)
N(2)–Pd–C(38)	117.9(3)	N(2)–C(1)–C(12)	117.4(6)
C(38)–Pd–C(39)	39.9(3)	N(1)–C(12)–C(1)	118.5(5)
Pd–N(1)–C(12)	112.7(4)	N(1)–C(12)–C(10)	135.0(6)
Pd–N(1)–C(25)	131.2(4)	Pd–C(38)–C(37)	106.4(6)
C(12)–N(1)–C(25)	116.1(5)	C(37)–C(38)–C(39)	106.8(7)
Pd–N(2)–C(1)	113.5(4)	Pd–C(39)–C(40)	108.7(6)
Pd–N(2)–C(13)	128.5(4)	C(38)–C(39)–C(40)	107.3(7)

N(2)–C(1)–C(12)–N(1)	–1.1(8)	C(26)–C(25)–N(1)–C(12)	–93.2(7)
C(2)–C(1)–C(12)–C(10)	–0.4(7)	C(30)–C(25)–N(1)–C(12)	84.9(7)
C(14)–C(13)–N(2)–C(1)	–76.9(8)	C(37)–C(38)–C(39)–C(40)	1.9(9)
C(18)–C(13)–N(2)–C(1)	105.6(7)		

by a combination of a rehybridization toward sp³ around the alkenic C atom upon coordination to the palladium and steric repulsion due to the o-isopropyl substituents on the aromatic group. The average Pd–N distance of 2.159(6) Å for **5c** is comparable to or somewhat shorter than those in other Pd–diimine systems, i.e. 2.194(4) Å in PdCl(Me)(9,10-Me₂Phen)(MA)[6a] and 2.164(8) Å in Pd(bpy)(DBA).[28] The average Pd–C(alkene) distance (2.064(8) Å) is shorter than those in other Pd(η²-alkene) complexes, i.e. 2.096(6) Å in PdCl(Me)(9,10-Me₂Phen)(MA),[6a] 2.087(9) Å in Pd(bpy)(DBA),[28] 2.23(2) Å in Pd(DBA)₃,[29] 2.26(1) Å in Pd₂(DBA)₃·CH₂Cl₂,[30] 2.25(1) Å in Pd₂(DBA)₃·CHCl₃,[17] and 2.130(3) Å in Pd(Cy₂PCH₂CH₂PCy₂)(η²-CH₂=CH—CH=CH₂).[31] The other distances and angles in the structure are as expected and showed no anomalies, except for one of the isopropyl groups which shows C(32)–C(31)–H(311) and C(33)–C(31)–H(311) angles of about 90°, due to static and/or dynamic disorder in the crystal.

UV/Vis and IR Spectroscopy. The UV spectra of the Pd(p-Tol-BIAN)(alkene) complexes **2a–d** all show two absorptions:

(28) Pierpont, C. G.; Buchanan, R. M.; Downs, H. H. *J. Organomet. Chem.* **1977**, *124*, 103.
(29) Mazza, M. C.; Pierpont, C. G. *Inorg. Chem.* **1973**, *12*, 2955.
(30) Pierpont, C. G.; Mazza, M. C. *Inorg. Chem.* **1974**, *13*, 1891.
(31) Benn, R.; Betz, P.; Goddard, R.; Jolly, P. W.; Kokel, N.; Krüger, C.; Topalovic, I. *Z. Naturforsch.* **1991**, *46B*, 1395.

Table 4. UV/Vis Data for Pd(p-Tol-BIAN)(alkene) Complexes 2a–d

	solvent	λ, nm		solvent	λ, nm
2a	THF	547	2a	toluene	560
2b	THF	478	2a	THF	547
2c	THF	468	2a	DMF	506
2d	THF	448	2a	CH₃CN	504

Table 5. IR Data for M(NN)(alkene) Complexes (M = Pd, Pt) in CH₂Cl₂ (cm⁻¹)

	ν(C=O)		ν(C=O)		ν(CN)		ν(CN)
1a	1687, 1675	7c	1797, 1727	1b	2200	9b	2201
2a	1684	8c	1795, 1724	2b	2201	10b	2203
3a	1690	9c	1796, 1725	3b	2200	11b	2205
1c	1796, 1726	10c	1801, 1730	4b	2202	12b	2203
2c	1795, 1724	11c	1802, 1735	5b	2203	1d	2226
4c	1797, 1728	12c	1800, 1732	6b	2200	2d	2225
5c	1800, 1728			7b	2203	10d	2225
6c	1798, 1729			8b	2199		

One at approximately 320 nm (an intraligand π–π* transition) and one in the visible region (Table 4). The wavelength of the transition in the visible region decreases with increasing solvent polarity, which is indicative of a metal-to-ligand charge transfer (MLCT) from a high-lying filled orbital localized on the palladium center to a low-lying empty orbital localized on the BIAN ligand. Comparison of complexes 2a–d in THF shows that the wavelength of the MLCT transition decreases in the order DMFU > FN > MA > TCNE, i.e. in the order of increasing electron accepting properties of the alkene (which can be derived from their electron affinities[32] and their electrochemical reduction potentials[33]).

The infrared spectra of the complexes in dichloromethane solution show a shift of the C=O and C≡N absorptions of the alkenes to lower wavenumber upon coordination (Table 5) and are in the range observed for other zerovalent palladium and platinum complexes.[10,34-39] The CN stretching vibrations of the diimine ligand could not be assigned, because they occur below 1600 cm⁻¹.

NMR Spectroscopy of Complexes Containing Symmetric Ligands (1–5, 10, 11). From both ¹H and ¹³C NMR data for the M(Ar-BIAN)(alkene) complexes 1–5a–d, 10, and 11b–d (Tables 6 and 7) it appears that the signals of the Ar-BIAN ligands shift to higher frequency upon coordination to the metal center, as compared to the free ligands,[12c] as is clearly seen for, e.g., H₄,₅ and C₁. Conversely, for the alkenic protons shifts of 3.0–3.5 ppm to lower frequency are observed in ¹H NMR, and for the alkenic C atoms shifts of 90–120 ppm to lower frequency are observed in the ¹³C NMR spectra.[40] These chemical shifts are in the range normally observed for other zerovalent ML₂(alkene) complexes (M = Pd, Pt) containing DMFU, FN, and MA, including complexes with isocyanide,[10c,35] alkene,[35,36] phosphine,[10a,34,37,38] phosphite,[39] diimine,[10e,f,39,41-43] and diamine[39] ligands. The DMFU complexes 1a and 2a are labile in solution and ¹³C NMR data

(32) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978, p 503.
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(38) (a) Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134. (b) Yoshida, T.; Yamagata, T.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063.
(39) Ito, T.; Hasegawa, S.; Takahashi, Y.; Ishii, Y. *J. Organomet. Chem.* **1974**, *73*, 401.
(40) ¹H (¹³C) NMR data for the free alkenes in CDCl₃: DMFU, 6.86 (133.9) ppm; FN, 6.29 (119.8) ppm; MA, 7.04 (137.1) ppm.
(41) Sustmann, R.; Lau, J.; Zipp, M. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 356.
(42) Cucciolito, M. E.; Panunzi, A.; Ruffo, F.; De Felice, V. *Gazz. Chim. Ital.* **1989**, *119*, 461 (1989).
(43) De Felice, V.; Funicello, M.; Panunzi, A.; Ruffo, F. *J. Organomet. Chem.* **1991**, *403*, 243.

could only be obtained at low temperatures ($T \le -20\,°$C), whereas complex 3a is too unstable in solution to obtain ¹³C NMR data, even at low temperatures. The ¹H NMR data of the DMFU complexes 1–3a show a remarkable shift to lower frequency of the carbomethoxy CH₃ upon coordination (to 3.3 ppm), whereas the chemical shift of this group in other zerovalent DMFU complexes usually varies between 3.48 and 3.60 ppm.[10e,f,35,36,39,42,43]

NMR Spectroscopy of Complexes Containing Asymmetric Ligands (6–9, 12). The M(Ph-BIC)(alkene) complexes (M = Pd (9b,c), Pt (12b,c)) and the Pd(Ar-BIAN)(alkene) complexes containing ortho- and meta-substituted Ar groups (6–8b,c) show the same features as described for the other M(Ar-BIAN)(alkene) complexes, i.e. shifts to higher frequency of the ligand signals and pronounced shifts to lower frequency for the alkene resonances, upon coordination to the metal center (supplementary material).
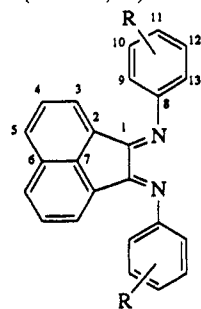
Because of the chirality of the Ph-BIC ligand, the complexes M(Ph-BIC)(FN) (9,12b) containing the E-alkene FN occur as two diastereoisomers, for palladium as well as platinum, in a ratio of 55:45, indicating little preference for the coordination to the si- or the re-face of FN. These diastereoisomers can only interconvert by dissociation of the alkene followed by recoordination to the metal center. On the other hand complexes of the Z-alkene MA, M(Ph-BIC)(MA) (9,12c), can occcur as two isomers which can interconvert by rotation of the alkene. In solution (mainly) one isomer is observed (9c (M = Pd) one isomer (>95%); 12c (M = Pt) two isomers in a ratio of 1:4), which is most likely the isomer with the anhydride group of the alkene pointing away from the CMe₂ bridge of the Ph-BIC ligand due to steric interactions.

9b, M = Pd; 12b, M = Pt
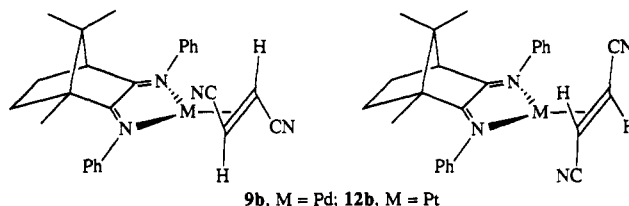
In the case of complexes containing o-tolyl or o-i-PrC₆H₄ groups on the imine N atoms (6,7b,c) a mixture of isomers is formed. Pd(o-i-PrC₆H₄-BIAN)(FN) 7b gives one AB pattern (2.82 d, 2.73 d, J = 9.5 Hz) and two singlets (2.80 s, 2.76 s) for the alkenic protons, indicating formation of a mixture of one C₁ symmetric and two C₂ symmetric complexes. The other ¹H NMR data (four doublets for H₅, two multiplets for C*H* (i-Pr) and eight doublets for C*H*₃ (i-Pr)) and ¹³C NMR data (four signals for C₁, C₃, C₈, C₉, C₁₃, and C*H* (i-Pr), eight signals for C*H*₃ (i-Pr) and three signals for alkenic C atoms) are in agreement with this assignment. Three isomers are also observed for the o-Tol-BIAN complexes 6b. From the observation of an AB pattern (3.78 d, 3.76 d, J = 3.7 Hz) and two singlets (3.80 s, 3.76 s) for the alkenic protons in ¹H NMR of Pd(o-i-PrC₆H₄-BIAN)(MA) 7c the presence of one C₁ symmetric and two C_s symmetric isomers was deduced. For Pd(o-Tol-BIAN)(MA) 6c only one broadened resonance at 4.0 ppm was observed for the alkene protons in ¹H NMR. On the other hand, for the m-Tol-BIAN complexes 8b and 8c only one set of resonances was observed in ¹H and ¹³C NMR in both cases, indicating the formation of one isomer or complete overlap of the resonances due to the different isomers.

Alkene Rotation in M(NN)(alkene) Complexes. Palladium and platinum compounds containing Ph-BIC (9,12b,c) or complexes containing Ar-BIAN in combination with MA (4,5c) show fluxional behavior on the NMR time scale. M(Ph-BIC)(FN) complexes (9,12b) show in the slow exchange limit two AB patterns for the alkene protons due to the asymmetry of the ligand and the presence of two diastereoisomers. For the palladium complex 9b, at higher temperatures, the signals broaden and coalesce,

Table 6. ¹H NMR Data for M(Ar-BIAN)(alkene) Complexes (M = Pd, Pt)[a]

	3	4	5	9, 13	10, 12	11	R	=CH (alkene)[b]
1a	7.25 d	7.46 pst	8.03 d	7.4 d	7.5 m	7.4 d	H	DMFU
	7.2 Hz		8.3 Hz	(6 H)	(4 H)	(6 H)		3.87 s
2a	7.36 d	7.46 pst	8.00 d	7.35 s	7.35 s	*	p-Me	DMFU
	7.2 Hz		8.1 Hz	(8 H)	(8 H)		2.47 s	3.86 s
3a	7.36 d	7.52 pst	8.08 d	7.33 d	7.66 d	*	p-Br	DMFU
	7.4 Hz		8.3 Hz	8.5 Hz	8.5 Hz			3.90 s
1b	7.33 d	7.6 m	8.08 d	7.6 m	7.6 m	7.6 m	H	FN
	7.3 Hz	(12 H)	8.2 Hz	(12 H)	(12 H)	(12 H)		2.86 s
2b	7.45 d	7.52 pst	8.06 d	7.36 d	7.45 d	*	p-Me	FN
	(6 H)		8.0 Hz	8.2 Hz	(6 H)		2.49 s	2.82 s
3b	7.42 d ·	7.58 pst	8.13 d	7.44 d	7.72 d	*	p-Br	FN
	7.1 Hz		8.3 Hz	8.5 Hz	8.5 Hz			2.87 s
4b	6.79 d	7.50 pst	8.07 d	*	7.25 s	7.25 s	o,o'-Me₂[c]	FN
	7.2 Hz		8.3 Hz		(6 H)	(6 H)		2.79 s
5b	6.71 d	7.48 pst	8.08 d	*	7.40 s	7.40 s	o,o'-i-Pr₂[d]	FN
	7.2 Hz		8.3 Hz		(6 H)	(6 H)		2.76 s
1c	7.37 d	7.52 pst	8.06 d	7.5 m	7.5 m	7.5 m	H	MA
	7.2 Hz		7.9 Hz	(10 H)	(10 H)	(10 H)		3.83 s
2c	7.42 d	7.49 pst	8.05 d	7.37 s	7.37 s	*	p-Me	MA
	7.3 Hz		8.0 Hz	(8 H)	(8 H)		2.48 s	3.85 s
4c	6.74 d	7.46 pst	8.07 d	*	7.21 s	7.21 s	o,o'-Me₂	MA
	7.2 Hz		8.3 Hz		(6 H)	(6 H)	2.28 br	3.73 s
5c	6.68 d	7.46 pst	8.04 d	*	7.36 s	7.36 s	o,o'-i-Pr₂[e]	MA
	7.1 Hz		8.3 Hz		(6 H)	(6 H)		3.74 s
1d	7.39 d	7.6 m	8.17 d	7.6 m	7.6 m	7.6 m	H	TCNE
	7.3 Hz	(12 H)	8.2 Hz	(12 H)	(12 H)	(12 H)		
2d	7.47 d	7.59 pst	8.15 d	7.42 d	7.47 d	* ·	p-Me	TCNE
	(6 H)		8.1 Hz	8.0 Hz	(6 H)		2.51 s	
10b	7.66 d	7.52 pst	8.18 d	7.40 d	7.63 d	*	p-Me	FN
	7.3 Hz		8.2 Hz	8.1 Hz	8.1 Hz		2.52 s	2.83 (91.2 Hz)
11b	6.82 d	7.47 pst	8.18 d	*	7.4 s	7.4 s	o,o'-i-Pr₂[f]	FN
	7.2 Hz		8.3 Hz		(6 H)	(6 H)		2.76 (93.1 Hz)
10c	7.65 d	7.50 pst	8.17 d	7.40 d	7.58 d	*	p-Me	MA
	7.3 Hz		8.3 Hz	8.0 Hz	8.0 Hz		2.52 s	3.65 (86.9 Hz)
11c	6.82 d	7.45 pst	8.19 d	*	7.4 s	7.4 s	o,o'-i-Pr₂[g]	MA
	7.2 Hz		8.3 Hz		(6 H)	(6 H)		3.59 (89.1 Hz)
10d	7.7 m	7.7 m	8.24 d	7.46 d	7.7 m	*	p-Me	TCNE
	(8 H)	(8 H)	8.0 Hz	7.8 Hz	(8 H)		2.55 s	

[a] Recorded at 300.13 MHz in CDCl₃ at 20 °C. Coupling constants (Hz) are given below the chemical shift values (* = position where the R-substituent is attached; s = singlet; d = doublet; pst = pseudo triplet; sept = septet; m = multiplet; br = broad). [b] DMFU complexes 1–3a show δ(OMe) at 3.31 s, 3.31 s, and 3.36 s, respectively. The coupling constants to ¹⁹⁵Pt for complexes 10 and 11 are shown in parentheses. [c] 2.40 s, 2.33 s. [d] 3.49 sept (6.8 Hz), 3.31 sept (6.9 Hz), CH; 1.50 d, 1.45 d (6.8 Hz), 1.07 d, 0.97 d (6.9 Hz), CH₃. [e] 3.33 br (4 H), CH; 1.41 d (12 H, 6.8 Hz); 1.03 d (6 H), 0.93 d (6 H, 6.9 Hz), CH₃. [f] 3.55 sept (6.7 Hz), 3.47 sept (6.8 Hz), CH; 1.50 d, 1.42 d (6.7 Hz), 1.03 d, 0.94 d (6.8 Hz), CH₃. [g] 3.46 m (4 H), CH; 1.40 pst (12 H), 1.04 d (6 H), 0.91 d (6 H, 6.8 Hz), CH₃.

finally leading to one signal (Figure 2). The two doublets of H₄ remain present in an unaltered ratio of 55:45 and do not show any broadening or interconversion.

The Pd(Ph-BIC)(MA) complexes (9c) show in the limit of slow exchange two slightly broadened signals for the alkene protons, which is probably due to the unresolved scalar coupling for the alkenic protons of the Z-alkene. The analogous platinum complex (12b) shows two AB patterns in a ratio of 1:4 due to the presence of the two rotamers. For complexes 4c and 5c, containing the Z-alkene MA and an ortho-disubstituted aromatic group, o,o'-Me₂C₆H₃ and o,o'-i-Pr₂C₆H₃, respectively, on the imine N-atom of the Ar-BIAN ligand, fluxional behavior on the NMR time scale was also observed. Due to the symmetry of the Ar-BIAN ligands the alkene protons remain isochronous both in the slow and in the fast exchange regime, thus giving one singlet at each temperature. However, when the Z-alkene MA was

coordinated, changes were observed in the signals of the ortho substituents on the aromatic ring, as these are inequivalent at slow alkene rotation and become averaged at fast alkene rotation. For the *E*-alkene FN, no changes in the signals of the ortho substituents was observed with variation of the temperature (293–333 K).

Variable temperature NMR data and estimated rotation barriers ($\Delta G^{\ddagger}_{rot}$) have been compiled in Table 8. Rotation barriers have been estimated from the coalescence temperature (T_c) by using the equation $\Delta G^{\ddagger}_{rot} = -RT_c \ln[\pi \Delta \nu h/(2^{1/2}kT_c)]$. By measuring rotation barriers for complex 4c at two different nominal frequencies (100.13 and 300.13 MHz, respectively), we have obtained two independent estimates of the rotation barrier, which were equal within experimental error. For the platinum complexes 12b,c and 11c the coalescence temperature could not be reached in chloroform. Experiments at higher temperatures

Table 7. ^{13}C NMR Data for M(Ar-BIAN)(alkene) complexes (M = Pd, Pt)^a

	1	2	3	4	5	6	7	8	9, 13	10, 12	11	R	=CR'	R'
1a^b	167.5	128.7	125.8	127.9	132.1	132.7	145.4	149.9	122.5	130.8	129.9	(H)	45.9 (DMFU)	175.5 (C=O)^c
2a^b	167.2	129.7	125.6	128.1	131.9	132.7	145.2	147.4	122.7	131.2	138.7	22.9 (p-Me)	45.5 (DMFU)	175.6 (C=O)^c
1b	167.3	126.8	125.2	128.4	131.5	132.0	145.2	149.2	121.4	130.3	129.0	(H)	22.0 (FN)	122.7 (CN)
2b	166.9	126.9	125.0	128.9	131.4	132.0	145.0	146.7	121.5	130.8	138.5	21.9 (p-Me)	21.3 (FN)	123.0 (CN)
3b	168.6	NO	126.5	130.2	133.1	134.4	146.3	148.7	127.1	132.8	123.0	(p-Br)	22.5 (FN)	124.1 (CN)
4b	168.5	128.3	124.5	129.3	131.8	133.7	144.5	147.1	127.0^d	129.7	127.1	e (o,o'-Me$_2$)	20.4 (FN)	122.7 (CN)
5b	169.0	127.2	125.1	129.4	131.8	131.9	144.4	145.3	138.3, 138.0	124.9, 124.6	127.9	f (o,o'-i-Pr$_2$)	20.9 (FN)	122.5 (CN)
1c	167.0	126.5	125.0	128.7	131.7	131.8	145.0	148.8	121.8	130.2	129.0	(H)	45.6 (MA)	172.4 (C=O)
2c	166.7	127.0	124.9	128.9	131.3	130.6	NO	146.5	121.9	130.7	138.8	21.9 (p-Me)	44.2 (MA)	172.4 (C=O)
4c	168.6	126.9	124.4	129.2	131.8	128.1	144.6	146.7	126.9	129.7	127.1	g (o,o'-Me$_2$)	43.0 (MA)	172.2 (C=O)
5c	168.8	127.2	125.0	129.4	131.8	131.9	144.4	145.0	138.5, 137.6	124.9, 124.5	127.9	h (o,o'-i-Pr$_2$)	43.6 (MA)	172.0 (C=O)
1d	170.3	125.5	126.3	129.4	133.0	132.0	147.0	147.8	121.2	130.9	129.8	(H)	NO (TCNE)	113.7 (CN)
2d	169.8	125.8	126.0	129.2	132.7	132.0	146.7	145.4	121.2	131.9	140.1	21.9 (p-Me)	NO (TCNE)	113.8 (CN)
10b	169.7	127.4	124.2	129.6	131.1	132.7	146.4	146.2	122.8	130.7	139.7	21.9 (p-Me)	1.9 (FN)	122.8 (CN)
11b	172.1	127.8	125.0	130.1	131.2	132.7	145.8	145.1	139.4, 139.1	124.7, 124.3	128.6	i (o,o'-i-Pr$_2$)	1.6 (FN)	124.4 (CN)
10c	170.9	128.5	125.0	130.4	131.8	133.5	144.8	147.0	124.1	131.5	140.8	22.9 (p-Me)	27.8 (MA)	173.9 (C=O)
11c	171.9	128.0	125.0	130.1	131.0	132.8	144.9	145.6	139.5, 138.8	124.5, 124.1	128.6	j (o,o'-i-Pr$_2$)	26.4 (MA)	174.6 (C=O)
10d	172.1	125.6	125.6	129.5	132.8	132.5	148.3	145.2	122.3	131.3	141.2	22.0 (p-Me)	NO (TCNE)	114.9 (CN)

^{a} Recorded at 75.48 MHz in CDCl$_3$ at 20 °C, unless noted otherwise. See the structure shown in Table 6 for the adopted numbering scheme (NO = not observed). ^{b} Recorded at –20 °C. ^{c} OMe resonances at 52.4 ppm. ^{d} Broad signal. ^{e} 18.6, 18.5 ppm. ^{f} 29.7, 29.6 ppm, CH; 24.2, 24.1, 24.0, 23.9 ppm, CH$_3$. ^{g} 18.5, 18.3 ppm. ^{h} 29.8, 29.4 ppm, CH; 24.2, 24.0, 23.8, 23.4 ppm, CH$_3$. ^{i} 29.4, 29.2 ppm, CH; 24.4, 24.3, 24.2, 24.1 ppm, CH$_3$. ^{j} 29.5, 29.1 ppm, CH; 24.4, 24.3, 24.1, 23.5 ppm, CH$_3$.
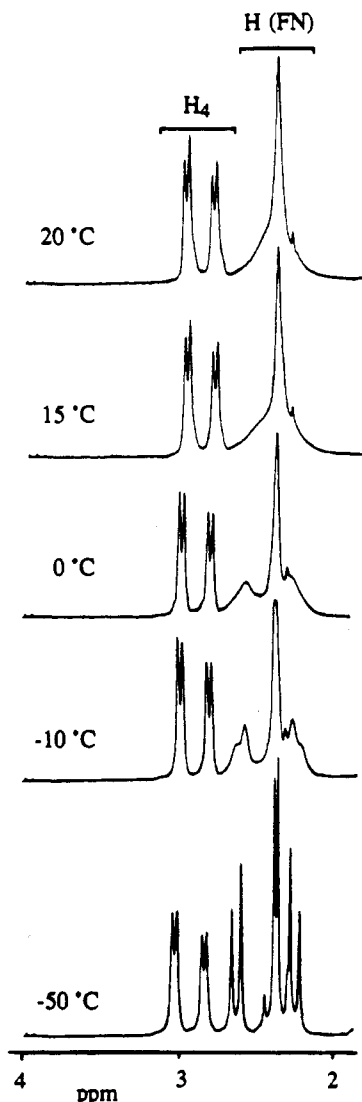

Figure 2. Variable-temperature ^1H NMR spectra of Pd(Ph-BIC)(FN) (9b) at 300.13 MHz in CDCl$_3$ (40 mM).

in bromobenzene-d_5 failed due to extensive decomposition at higher temperatures ($T > 340$ K), resulting in deposition of metallic platinum and the formation of free alkene in solution, which both lead to line broadening in the NMR spectra. From

**Table 8.** Variable-Temperature ^1H NMR Data and Calculated Alkene Rotation Barriers^a

	$\Delta\nu$, Hz	T_c, K	$\Delta G^\ddagger_{rot}$, kJ/mol
Pd(o,o'-Me$_2$C$_6$H$_3$-BIAN)(MA) (4c)	2.46^b	293	67.6
	7.37^c	308	68.4
Pd(o,o'-i-Pr$_2$C$_6$H$_3$-BIAN)(MA) (5c)	10.12^b	313	68.7
Pt(o,o'-i-Pr$_2$C$_6$H$_3$-BIAN)(MA) (11c)	2.92^b	>333	>77
Pd(Ph-BIC)(FN) (9b)			
minor isomer	12.85^c	264	57.0
major isomer	57.64^c	288	58.8
Pd(Ph-BIC)(MA) (9c)	36.11^c	245	50.7
Pt(Ph-BIC)(FN) (12b)	8.30^b	>333	>74
Pt(Ph-BIC)(MA) (12c)	18.85^b	>333	>72

^{a} Measurements were carried out with 40 mM solutions in CDCl$_3$. Rotation barriers were calculated from the coalescence temperature (T_c) and the frequency difference between the coalescing signals in the limit of slow exchange ($\Delta\nu$ in Hz) with the formula $\Delta G^\ddagger_{rot} = -RT_c \ln[\pi\Delta\nu h/(2^{1/2}kT_c)]$. Coalescence temperatures are determined within 3 K accuracy. The estimated error in the calculated rotation barriers is 0.7–1.0 kJ/mol. ^{b} Recorded at 100.13 MHz. ^{c} Recorded at 300.13 MHz.

the data ($T > 333$ K in all cases) the lower limits of the alkene rotation barriers in the Pt(alkene) complexes were estimated, and these barriers were higher than those of comparable palladium complexes in all cases.

Alkene Substitution and Alkene Exchange in M(NN)(alkene) Complexes. The alkene coordinated to the metal center in M(NN)(alkene) complexes can be readily substituted in solution by another alkene, and the reaction is generally completed within several minutes at 20 °C in THF, acetone, or CDCl$_3$. From these reactions of palladium complexes containing Ph-BIAN or p-Tol-BIAN ligands (1,2) it appeared that DMFU was substituted quantitatively by 1 equiv of any of the other alkenes and that all of the other alkenes were quantitatively substituted by 1 equiv of TCNE. Addition of 1 equiv of MA to Pd(Ph-BIAN)(FN) (1b) or 1 equiv of FN to Pd(Ph-BIAN)(MA) (1c) led to a mixture of 1b and 1c in a ratio of 14:86 in both cases, indicating that equilibrium has been reached. Complexes containing an o-isopropyl substituted BIAN ligand (5,7) show increased affinity for FN as compared to complexes with unsubstituted or para-substituted Ar-BIAN ligands (1,2): reaction of Pd(o-i-PrC$_6$H$_4$-BIAN)(FN) 7b with 1 equiv of MA gave 7b and 7c in a ratio of 31:69 and reaction of Pd(o,o'-i-Pr$_2$C$_6$H$_3$-BIAN)(FN) 5b with 1 equiv of MA gave 5b and 5c in a ratio of 47:53. Reactions of the analogous MA complexes 5c and 7c with 1 equiv of FN gave the same compositions of the reaction mixtures, indicating formation of equilibrium mixtures in all cases. Complete
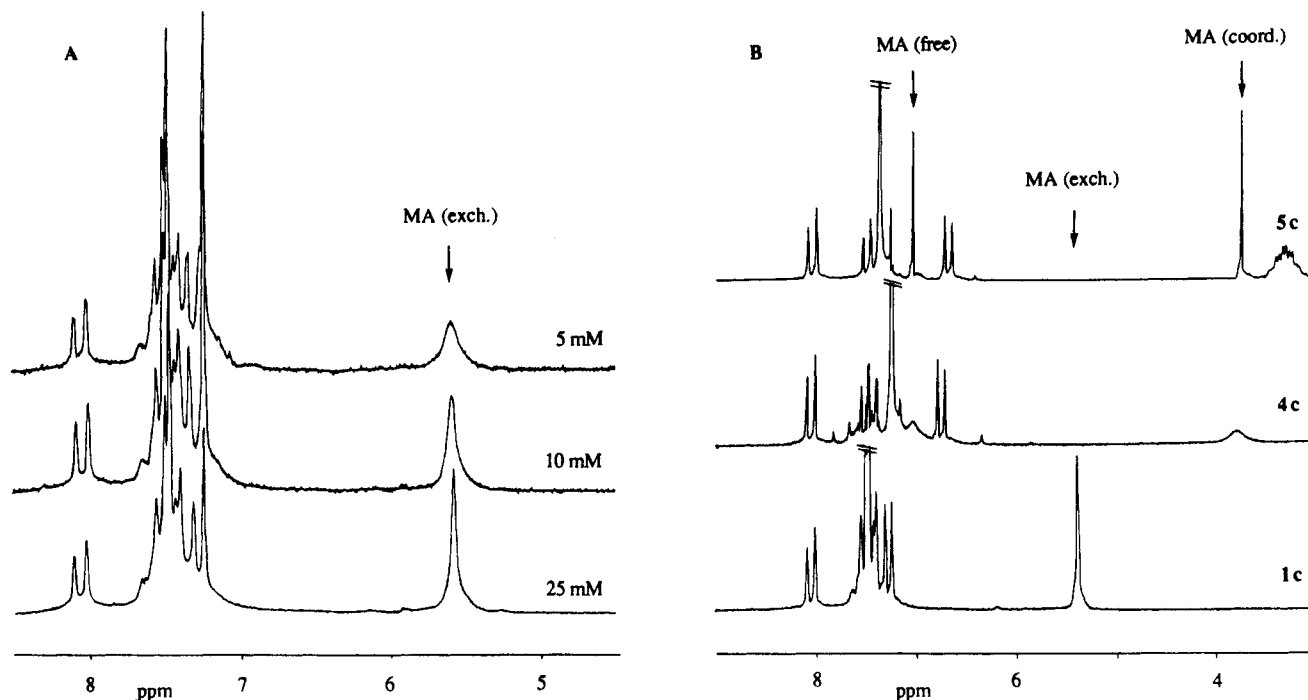
Figure 3. ^{1}H NMR spectra of Pd(Ar-BIAN)(MA) complexes in CDCl$_3$ at 100.13 MHz in the presence of 1 equiv of MA: (A) Pd(Ph-BIAN)(MA) (**1c**), various concentrations at 20 °C; (B) Pd(NN)(MA) (**1, 4, 5c**), influence of the steric crowding of Ar-BIAN, 40 mM solutions at 20 °C.

substitution of the coordinated alkene could be achieved by reaction of the zerovalent complex with a 10-fold excess of alkene.

Interestingly, exchange of alkenes was also observed in the reaction of two different Pd(NN) (alkene) complexes, e.g. **1b** and **5c**, in the absence of free alkene. In this case exchange was much slower than with free alkene (about 1.5 h). A mixture of all four possible products **1b**, **1c**, **5b**, and **5c** in an approximate ratio of 1:1:1:1 was formed, and there was no evidence for any decomposition (i.e. no formation of metallic palladium, free alkene, or free Ar-BIAN). In the presence of free alkene the Pd(*p*-Tol-BIAN)(alkene) and Pd(Ph-BIAN)(alkene) complexes show fast exchange on the NMR time scale between coordinated and free alkene, similar to what has been described for Pd(bpy)-(FN),[41] the rate of which decreases with decreasing concentration of the complex and of the alkene. Furthermore increased steric bulk of the Ar group of the Ar-BIAN ligand decreases the rate of exchange, as shown for the MA complexes **1**, **4**, and **5c** (Figure 3).

In the ^{1}H NMR spectrum of Pd(Ph-BIC)(FN) (**9b**) in the presence of 1 equiv of FN, the signals of H$_4$ due to the two diastereoisomers initially present coalesce to one signal. Rapid substitution of the coordinated FN by free FN, which can either coordinate via its si- or re-face, accounts for the interconversion between the two diastereoisomers.

Ligand Substitution Reactions. Reaction of Pd(*p*-Tol-BIAN)-(MA) (**2c**) with 1 equiv of *o,o'-i*-Pr$_2$C$_6$H$_3$-BIAN in CDCl$_3$ leads to substitution of the *p*-Tol-BIAN, giving a mixture of **2c** and **5c** in a ratio of 65:35. The same mixture is obtained when Pd-(*o,o'-i*-Pr$_2$C$_6$H$_3$-BIAN)(MA) **5c** is reacted with *p*-Tol-BIAN, indicating that this is the thermodynamic equilibrium mixture. In both cases the substitution of the Ar-BIAN ligand is much slower than substitution of the alkene and equilibrium is reached after several hours.

Reaction of Zerovalent Complexes with Alkynes. From reactions of Pd(DBA)$_2$ with alkynes no zerovalent complexes of the type Pd(Ar-BIAN)(η^2-alkyne) could be obtained. In the case of dimethyl butynedioate (DMBD), i.e. an alkyne containing strongly electron-withdrawing substituents, a cyclization reaction

occurs, leading to a palladacyclopentadiene complex, **13**, similar to complexes containing other nitrogen or phosphine ligands.[44,45]

13
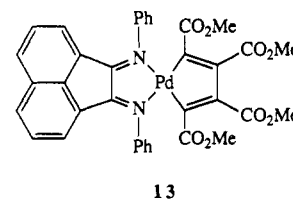
Even short reaction times at –40 °C or reaction in an apolar solvent like benzene resulted in the formation of the palladacy-clopentadiene complex **13** as the only product. Reactions with less than 2 equiv of DMBD led to mixtures of starting materials and **13**, whereas **13** was formed together with the cyclotrimer-ization product from DMBD, hexamethyl mellitate, when an excess DMBD was used (>2 equiv to Pd). It has been described before that stronger σ-donating ligands favored the formation of the palladacyclopentadiene instead of the Pd^0(η^2-alkyne) com-plex.[46] Reactions of Pd(DBA)$_2$ with diphenyl acetylene or 3-hexyne in the presence of Ar-BIAN gave neither a pallada-cyclopentadiene nor a Pd^0(η^2-alkyne) complex.

Discussion

Structure and Bonding of the Pd(NN)(alkene) Complexes. The structure of the alkene is completely modified upon coordination to the Pd(NN) and Pt(NN) fragment, which can be derived from the elongation of the C=C bond of about 0.11 Å in the crystal structure and the large shifts of the signals of the alkenic protons and C-atoms to lower frequency in the NMR spectra. These changes are due to a considerable amount of electron donation from the palladium to the alkene caused by the

(44) (a) tom Dieck, H.; Munz, C.; Müller, C. *J. Organomet. Chem.* **1987**, *326*, C1. (b) tom Dieck, H.; Munz, C.; Müller, C. *J. Organomet. Chem.* **1990**, *384*, 243. (c) Munz, C.; Stephan, C.; tom Dieck, H. *J. Organomet. Chem.* **1990**, *395*, C42.

(45) Maitlis, P. M. *Pure Appl. Chem.* **1972**, *30*, 427 (1972).

(46) (a) Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1971**, 1604. (b) Ito, T.; Hasegawa, S.; Takahashi, Y.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1972**, 629.

combination of an electron rich d^{10} metal center with a σ-donating diimine ligand. Back-donation of charge from the metal center to the alkene is the major factor in determining the stability of the metal–alkene bond as can be derived from (i) the finding that electronpoor alkenes are necessary in order to obtain stable, isolable complexes and (ii) the finding that the order of increasing thermodynamic stability of the complexes, DMFU < FN < MA < TCNE is also the order of increasing electron accepting properties of the alkenes.[32,33] The increasing amount of charge donation to the alkene in this series is reflected in the UV/vis data of the Pd(*p*-Tol-BIAN)(alkene) complexes **2a–d**. The increased donation of charge to the alkene leads to a decreased energy of the palladium-localized HOMO, whereas the *p*-Tol-BIAN localized LUMO can be expected to be less affected, which leads overall to a larger HOMO–LUMO separation and hence to a shift to shorter wavelength for the MLCT transition. The buildup of negative charge on the alkene is apparent from IR spectroscopy, as the CN stretching mode of coordinated TCNE (2225 cm^{-1}) is in between that of free TCNE (2250, 2237 cm^{-1}) and that of the TCNE anion (2200 cm^{-1}).[10e] The importance of back-donation is also apparent from the observation that the shifts of the alkenic protons and C atoms to lower frequency in NMR are more pronounced for the platinum than for the palladium complexes. This can be ascribed to the higher basicity of platinum as compared to palladium (see, e.g, ref 4c) and can be evaluated too from the chemical shift values reported in the literature for comparable PdL$_2$(alkene) and PtL$_2$(alkene) complexes.[10c,34–36] The higher basicity of platinum was also reflected by the fact that stable Pt(NN)(DMFU) complexes with Ar-BIAN and Ph-BIC ligands could not be synthesized and more electron withdrawing alkenes like FN, MA, and TCNE were needed.

The Ar-BIAN and Ph-BIC ligands act more as a σ-donor than as a π-acceptor to the palladium, as can be inferred from the minor changes of the C=N bond lengths of o,o'-i-Pr$_2$C$_6$H$_3$-BIAN upon coordination and the observed shifts in NMR to higher frequency upon coordination. Accordingly, the largest shifts toward higher frequency for the Ar-BIAN signals (e.g of H$_5$ and C$_1$) have been observed for complexes containing the most electron-withdrawing alkene, TCNE. From these data it appears that the rigid Ar-BIAN and Ph-BIC ligands are comparable to the open chain R-DAB analogues in electronic properties,[10e] which is in agreement with out earlier findings that the diimine system in the Ar-BIAN ligands is electronically isolated from and shows no conjugation with the naphthalene backbone.[12c] The higher σ-donating capabilities of Ar-BIAN ligands as compared to bpy appears from the fact that stable Pt(Ar-BIAN)(DMFU) and Pd(Ar-BIAN)(DBA) complexes could not be isolated, whereas stable Pt(bpy)(DMFU) and Pd(bpy)(DBA) complexes can be obtained. Apart from electronic factors, steric factors also influence the stability of the complexes, as can be derived from the observation that the affinity of M(Ar-BIAN) fragments for the smaller FN, as compared to MA, increases in the order *p*-Tol-BIAN < o-i-PrC$_6$H$_4$-BIAN < o,o'-i-Pr$_2$C$_6$H$_3$-BIAN, i.e. with increasing steric bulk of the Ar-BIAN ligand.
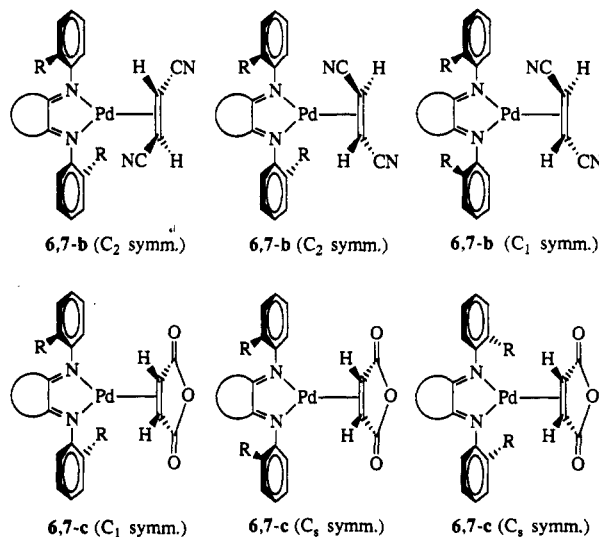
From a comparison of the chemical shift of the coordinated alkenes DMFU, FN, and MA with their saturated analogues dimethyl succinate, succinonitrile, and succinic anhydride, which show ^{1}H resonances at 2.62, 2.71, and 2.99 ppm, respectively, it becomes clear that the alkenic signals have shifted to the aliphatic region upon coordination. This suggests that the complexes possibly have to be regarded rather as M(II)–cyclopropane complexes than as M^0(η^2-alkene) complexes. This view is further corroborated by the observed values for the ^{195}Pt–C*H*(alkene) coupling constants (80–100 Hz), which are larger than those in complexes containing phosphine (about 60 Hz),[10a,38] isocyanide (62 Hz),[35] or diene (76 Hz)[35] ligands and are comparable to complexes containing α-diimine ligands (78–93 Hz).[43] These large coupling constants are in the range of ^{195}Pt–H$_\alpha$ coupling

constants of Pt–σ-alkyl complexes[47] and thus point at a considerable σ-character of the bond between the alkenic C atoms and the platinum center. The observed Pd–C bond lengths of **5c**, which are close to those observed for Pd–Me complexes with the methyl group bonded *trans* to a N atom,[12c,48,49] are also in agreement with the cyclopropane structure.

From the crystal structure of Pd(o,o'-i-Pr$_2$C$_6$H$_3$-BIAN)(MA) (**5c**), it is apparent that in the solid state the aromatic groups on the imine N atoms of Ar-BIAN are out of the coordination plane formed by the M(NN)(alkene) moiety, similar to what was observed for the uncoordinated *p*-Tol-BIAN.[12c] This orientation of the aromatic group is maintained in solution as can be deduced from the low-frequency shift of H$_3$ in ^{1}H NMR. In the ^{1}H NMR of the DMFU complexes **1–3a** this noncoplanarity of the aromatic group is also reflected in the shift of the methylester resonance to lower frequency, caused by the orientation of the methyl toward the aromatic group, imposed by the coordination of the double bond, and concomitant anisotropic shielding.


1-3 a
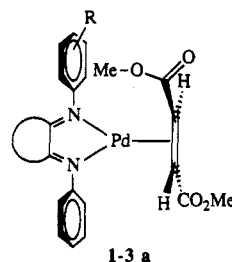
Complexes Containing Asymmetric Ar-BIAN Ligands (6,7). Formation of several isomers for complexes **6,7b,c** containing o-Tol-BIAN and o-i-PrC$_6$H$_4$-BIAN ligands can be ascribed to coordination of these ligands in both the *syn* and the *anti* conformation, similar to the observations made for Pd(Me)Cl-(Ar-BIAN) complexes.[12c]

6,7-b (C$_2$ symm.) 6,7-b (C$_2$ symm.) 6,7-b (C$_1$ symm.)

6,7-c (C$_1$ symm.) 6,7-c (C$_s$ symm.) 6,7-c (C$_s$ symm.)

Coordination of the o-i-PrC$_6$H$_4$-BIAN ligand in the *anti* form leads to the formation of two C$_2$ symmetric isomers for Pd(*o*-

(47) ^2J(Pt–H) values reported for Pt^{II}(NN)(CH$_2$R)$_2$ complexes are in the range 84–97 Hz: (a) Kuyper, J. *Inorg. Chem.* **1977**, *16*, 2171. (b) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 1538. (c) Griffiths, D. C.; Young, G. B. *Organometallics* **1989**, *8*, 875. (d) Anderson, C. M.; Crespo, M.; Jennings, M. C.; Lough, A. J.; Ferguson, G.; Puddephatt, R. J. *Organometallics* **1991**, *10*, 2672. (e) Anderson, C. M.; Crespo, M.; Ferguson, G.; Lough, A. J.; Puddephatt, R. J. *Organometallics* **1992**, *11*, 1177. (f) van Asselt, R.; Rijnberg, E.; Elsevier, C. J. *Organometallics* **1994**, *13*, 706.

(48) Byers, P. K.; Canty, A. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1990**, *393*, 299.

(49) de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907.

Scheme 1

Scheme 2
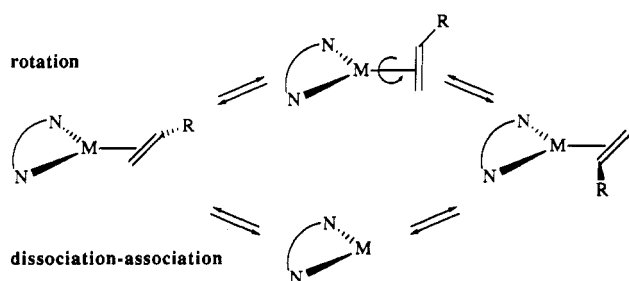
i-PrC₆H₄-BIAN)(FN) (**7b**) and one C_1 symmetric isomer for Pd(*o*-*i*-PrC₆H₄-BIAN)(MA) (**7c**). The formation of one C_1 symmetric isomer of **7b** and two C_s symmetric isomers of **7c** must be ascribed to coordination of *o*-*i*-PrC₆H₄-BIAN in the *syn* form. Formation of one C_1 symmetric isomer of **7b** could also be explained by coordination of the *o*-*i*-PrC₆H₄-BIAN ligands in the *anti* form and (i) *E* to *Z* isomerization of FN to succinonitrile (*Z/E* isomerization was observed for some alkenes with Pt(0) complexes[35]), (ii) coordination of FN via CN instead of via C=C,[50] and (iii) deviation from trigonal planarity, as proposed for Pd(PPh₃)₂(diethyl fumarate).[37] However, the observed chemical shifts and the coupling constants for **7b** in ¹H NMR are characteristic of an *E* alkene and coordination via the C=C double bond (cf. Pd(Ph-BIC)(FN) (**9b**)), and deviation from trigonal planarity can not explain the formation of two C_s symmetric isomers of **7c**.

Alkene Rotation in M(NN)(alkene) Complexes. The fluxional behavior of the zerovalent M(NN)(alkene) complexes can in principle be described by alkene rotation or by a dissociation–association mechanism (Scheme 1). The dissociation–association mechanism can be excluded by the observations that no inter-conversion between the diastereoisomers of Pd(Ph-BIC)(FN) (**9b**) is observed during exchange of the alkene protons and that no fluxional behavior for the FN complexes **4b** and **5b** is observed, which are both expected if dissociation–association would occur. The observation of facile alkene rotation seems to be in disagreement with the palladacyclopropane structure, but facile alkene rotation was also observed for Ru(η⁵-C₅Me₅)(acetyl-acetonato)(C₂F₄) ($\Delta G^{\ddagger}_{rot}$ = 55 ± 2 kJ/mol), which was shown to have merely a metallacyclopropane structure.[51]

From the data in Table 8 it is clear that the rotation barriers of the Ar-BIAN complexes **4c** and **5c** are higher than those of the Ph-BIC complexes **9b** and **9c**, which is due to the steric hindrance of the ortho substituent (from the NMR data it appears that the electronic properties of these ligands are comparable). The important contribution from steric factors to the rotation barriers of metal–alkene complexes is known, especially in square planar Pd(II) and Pt(II) complexes.[52] The higher rotation barriers of the alkenes in platinum complexes, as compared to analogous palladium complexes, might be due to the greater amount of donation of electron density from the metal to the alkene in platinum complexes, leading to a stronger metal–alkene bond in the coordination plane (which might increase the energy difference between the in-plane and out-of-plane orientation of the alkene and thereby the activation energy for alkene rotation).

Rotation of alkenes coordinated to Pd(0) and Pt(0) has been described before,[10f,35] but quantitative data are scarce.[53] The rotation barriers that we have found for palladium complexes **4,5**
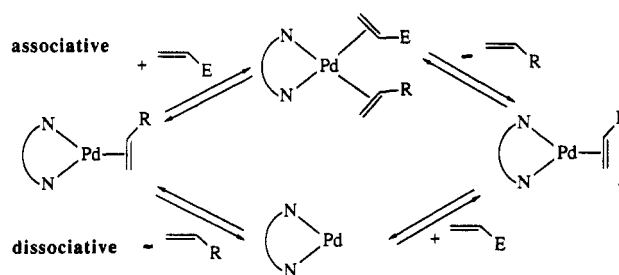
c and **9b,c** (50–69 kJ/mol) are comparable to those found for PdX₂(CH₂=CHMe)(2,9-Me₂Phen) (about 60 kJ/mol).[5f] The rotation barrier of the platinum complexes **11c** and **12b,c** (>72 kJ/mol) is higher than that observed for Pt(C₂H₄)₂(phosphine) complexes (40–55 kJ/mol).[53] This is probably due to the difference in electronic properies of the coordinated alkene, since it was shown that in the complex Pt(C₂F₄)(C₂H₄)(phosphine) the C₂H₄ is fluxional whereas the electron-withdrawing C₂F₄ is rigid. Larger rotation barriers for alkenes containing electron-withdrawing substituents have also been observed for [Ru(η⁵-C₅H₅)(*i*-Pr-DAB)(alkene)] SO₃CF₃ complexes.[54] The observed rotation barrier for the zerovalent platinum complexes is higher than that observed for square planar Pt(II) complexes of the type Pt(acac)Cl(alkene) and PtCl₂(alkene)(phosphine) (40–65 kJ/mol)[55] and for the five-coordinated complexes PtX₂(alkene)(*t*Bu-DAB) (55–65 kJ/mol)[56] and Pt(η⁵-C₅H₅)(C₂H₄)(PPh₃) (55 kJ/mol).[4c]

Substitution Reactions in M(NN)(alkene) Complexes. The mechanism of alkene substitution can either be a dissociative or an associative process (Scheme 2). The observed dependency on both the absolute concentration of the complex and of the alkene as well as the influence of ortho substitution on the aromatic group on the imine N atom (Figure 3) indicates an associative mechanism of alkene substitution, i.e. via a 18-electron Pd(NN)-(alkene)₂ complex, which is in agreement with the proposed associative mechanism of alkene exchange in Pt(PPh₃)₂(C₂H₄)[57] and Pd(PMePh₂)₂(alkene) complexes[58] and the mechanism of substitution of coordinated acetylenes in Pt(PPh₃)₂(acetylene) complexes.[59]

The observed decrease of the rate of substitution with increased ortho-substitution on the aromatic group can be ascribed to steric repulsions upon approach of a second alkene to the Pd(Ar-BIAN)-(alkene) complex, hindering formation of the Pd(NN)(alkene)₂ intermediate. Thus within the complex Pd(*o,o'*-*i*-Pr₂C₆H₃-BIAN)(MA) (**5c**) the exchange between coordinated and free MA is slow on the NMR time scale, due to a blocking or hindering of the associative pathway. However, as described above, there is an exchange between coordinated and free MA and FN which is completed within 10 min. This reaction can occur either via a slow associative or a dissociative mechanism.

Evidence for a dissociative mechanism comes from the reaction of two palladium complexes Pd(*p*-Tol-BIAN)(FN) (**1b**) and Pd-(*o,o'*-*i*-Pr₂C₆H₃-BIAN)(MA) (**5c**) in the absence of uncoordinated alkene, which led to the exchange of coordinated alkenes to give a mixture of **1b**, **1c**, **5b**, and **5c**. This exchange reaction occurs via initial dissociation of a coordinated alkene, indicating

(50) Coordination of FN via a CN group to ruthenium is known: de Klerk-Engels, B.; Hartl, F.; Vrieze, K.; Goubitz, K.; Fraanje, J. To be submitted for publication.

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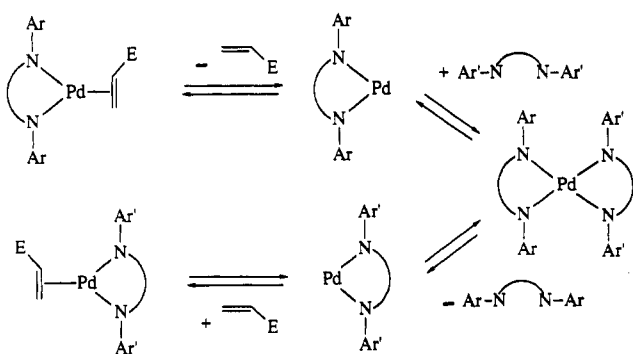
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Scheme 3

the possibility of dissociative reactions of Pd(Ar-BIAN)(alkene) complexes. Dissociative loss of coordinated alkenes from zerovalent ML$_2$(alkene) complexes (M = Ni, Pd, Pt) has been observed before.[39,57] In principle substitution might also occur via a binuclear complex, but this is unlikely because of steric reasons, especially if ligands with *o*-isopropyl substituents are present, and in view of the observed insensitivity of the rate of exchange to the concentration of the palladium complexes. Occurrence of both associative and dissociative pathways for substitution reactions at a platinum(0) phosphine complex has been reported.[60]

Dissociation of the alkene from Pd(NN)(alkene) complexes is most likely also the first step in the substitution of an Ar-BIAN ligand, e.g. in the reaction of Pd(*p*-Tol-BIAN)(MA) **2c** with *o,o'-i*-Pr$_2$C$_6$H$_3$-BIAN. Substitution via initial dissociative loss of the coordinated Ar-BIAN ligand is very unlikely in view of the highly unsaturated 12-electron Pd(alkene) intermediate, and substitution via an associative mechanism is unlikely in view of the severe steric hindrance in a four- or five-coordinate Pd(Ar-BIAN)(Ar'-BIAN)(alkene) complex, especially if one of the Ar-BIAN ligands is the sterically hindered *o,o'-i*-Pr$_2$C$_6$H$_3$-BIAN. Hence, the most likely pathway is initial dissociation of the alkene, followed by coordination of a second Ar'-BIAN to palladium (Scheme 3). The intermediate Pd(Ar-BIAN)(Ar'-BIAN) complex, the formation of which was inferred from electrochemical studies,[61] can lose either of the two Ar-BIAN ligands followed by recoordination of the alkene, regenerating the starting complex or producing the new complex.

Conclusion

A variety of zerovalent palladium and platinum complexes of the type M(NN)(alkene), containing the rigid bidentate nitrogen

ligand Ar-BIAN or Ph-BIC, has been synthesized and characterized. Stable complexes were only obtained for alkenes containing electron-withdrawing substituents, such as DMFU, FN, MA, and TCNE. Spectroscopic data (IR, UV–vis, ^{1}H and ^{13}C NMR) indicate that the nitrogen ligands act merely as σ-donors, whereas the alkenes act as good electron acceptors, indicating that the complexes might be regarded as M(II) metallacyclopropane structures. However, the reactivity of the complexes toward substitution of the coordinated alkene and the observed propellor rotation of the alkene showed the typical M(0)–alkene character of the complexes.

By the appropriate choice of the ligands coordinated to the metal center, important mechanistic information concerning alkene substituion and alkene rotation was obtained. For example, by using the chiral Ph-BIC ligand in combination with the prochiral alkene FN coordinated to palladium or platinum, it was demonstrated that the observed fluxional behavior could not be due to a dissociation–association sequence, leaving propellor rotation as the only alternative. Furthermore, the mechanism of alkene substitution was shown to depend on the steric requirements of the aromatic substituent of the Ar-BIAN ligand coordinated to the palladium center, changing from an associative mechanism for sterically unhindered ligands to a dissociative mechanism for the highly hindered *o,o'-i*-Pr$_2$C$_6$H$_3$-BIAN ligand. The availability of a variety of Ar-BIAN ligands and the facile synthesis of series of complexes containing these ligands has given us the opportunity to investigate reaction mechanisms of organometallic reactions and the influence of subtle changes of the ligands on these reactions. Further results illustrating this latter point will be published in forthcoming papers.[14,47f,62]

Supplementary Material Available: Tables of analytical data of complexes **1–12** (Table S1), ^{1}H and ^{13}C NMR data of complexes **6–9** and **12** (Tables S2–S5), and crystal data and details of the structure determination, (an)isotropic thermal parameters, bond distances and bond angles of the non-hydrogen atoms, and hydrogen positions and isotropic thermal parameters for Pd(*o,o'-i*-Pr$_2$C$_6$H$_3$-BIAN)(MA) (**5c**) (15 pages). Ordering information is given on any current masthead page.

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