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Electron Exchange Along the Tercyclopentadienyltrimetallic Scaffold: Kinetics, Equilibria, and Bond Strengths**

J. Kevin Cammack, Hani Amouri, Philip W. Leonard, Randy L. Myrabo, and K. Peter C. Vollhardt*

___Electron transfer is fundamental to chemical reactivity.[1] A prototype example in organometallic chemistry is the attack of an anionic metal center on a metal–metal bond, $M^- + M'–M'$, which, by nucleophilic substitution, should lead to $M–M' + M'^-$. Such is not cleanly found, however, the outcome of this mechanistically complex transformation usually being controlled by thermodynamic factors through electron redistribution to eventually provide $M–M + M'^-$.[2] We report the first direct observation of such equilibria for cyclopentadienyl (Cp) metals by NMR, mechanistic studies, and the utilization of the data in the estimation of CpM–M'Cp bond strengths. Key to these results is the employment of the tercyclopentadienyl ligand as a frame on which to render the desired transformations intramolecular and regiospecific (Scheme 1).[3]

___The required materials were made according to described protocols (Table 1),[3, 4] with a minor modification for the preparation of the anions **1–4**, **7**, **8**, and **9,** which, to avoid (competing) reduction of the metal–metal bond, were generated using NaH or (for **9**) *tert*–BuOK. Structural proof of all new compounds rested on spectral data, conversion to stable methyl derivatives (in the case of the anions), and X–ray analyses of **3** and **4**. Particularly diagnostic were the ^{1}H NMR spectra, which could be assigned, as appropriate, by comparison with known systems or known substructures,[3] by exploiting the effect of the anisotropy of a metal–metal bond on the δ values of the

A   **B**
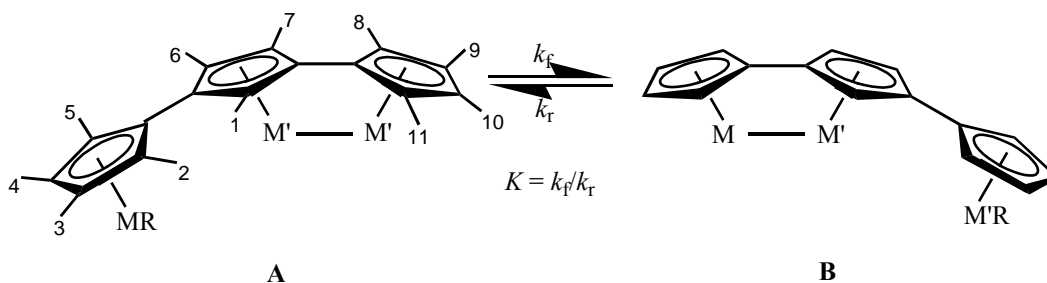
1, M = M' = Mo(CO)$_3$, R = −

2, M = W(CO)$_3$, M' = Mo(CO)$_3$, R = −

3, M = Mo(CO)$_3$, M' = W(CO)$_3$, R = −

4, M = M' = W(CO)$_3$, R = −

5, M = W(CO)$_3$, M' = Mo(CO)$_3$, R = H

6, M = Mo(CO)$_3$, M' = W(CO)$_3$, R = H

7, M = Cr(CO)$_3$, M' = Mo(CO)$_3$, R = −

8, M = Cr(CO)$_3$, M' = W(CO)$_3$, R = −

9, M = Mo(CO)$_3$, M' = Ru(CO)$_2$, R = −

10, M = Mo(CO)$_3$, M' = Ru(CO)$_2$, R = H

11, M = W(CO)$_3$, M' = Ru(CO)$_2$, R = H

12, M = Mo(CO)$_3$, M' = Ru(CO)$_2$, R = CH$_3$

Scheme 1. Tercyclopentadienyl complexes investigated in this work.

attached fulvalene (Fv) nuclei,[5] via the characteristic three- (~ 3 Hz) and four-bond (~

1.7 Hz) couplings in CpMs,[5b,c] by the occurrence of [183]W satellite signals, by way of the

distinctive hydride absorptions, and through 2D-NOESY, TOCSY, COSY, and (in the

case of rapid **A/B** exchange) EXSY experiments (vide infra). Corroborating ^{13}C NMR

data were particularly advantageous, especially in confirming the metal connectivity of

the CO ligands.[6] The IR absorptions for the pendant CO groups revealed the composite

patterns reflective of the individual FvM–M[(')] and CpM[(')] pieces, including ion

association for the alkali salts of the anions,[7] the local symmetry of which could be

restored by conversion to their ammonium analogues.[8]

___While delocalized renditions of anion **1** and its congeners are conceivable, the

spectral data indicate largely localized arrays. Nevertheless, some of the negative charge

on the isolated CpM[-] segment appears to spread to the formally neutral neighbor, as

evidenced by comparison with the properties of methylated relatives, e.g. **1-4**, R = CH$_3$,

and **12**. In particular, H1,6-11 in the anions resonate at higher field than in their

methylated relatives by an average of 0.15 ppm, and the corresponding dinuclear metal

carbonyl stretching frequencies are attenuated by an average of ~6 cm^{-1}. At the same

time, charge depletion of the anionic center is indicated by more energetic CO bands

(~11 cm^{-1}) than those measured for free CpM(CO)$_3$[-].[7b]

___To define conclusively the relationship of the metals in the anions and to probe

whether there are structural consequences of this charge delocalization, especially for the

metal–metal bond, X-ray crystallographic analyses were performed on **3-** and **4-**

Na^{+}•(THF)$_5$. Their gross topologies were found to be almost identical to each other and

to the known methylated **4** (R = CH$_3$), [3b] most notably marked by the anti-configuration

of the terCp sequence. Indeed, both compounds crystallize in the same space group *P*2$_1$

(no. 4) and are isomorphous. Because of problems with the data set for the structural

solution of **4**, only **3** is described (Figure 1). The compound exists as a cocrystallisate in

the thermodynamic (vide infra) ratio of the two isomers **A** and **B** and was successfully

modeled as such.[9] The structural details for the FvM–M$^{(')}$ fragment (e.g., the

intermetallic distance) are, within experimental limits, very similar to those of the

completely charge localized methyl derivative,[3b] whereas the anionic CpM part

resembles (e.g. average M–CO bond lengths) that of $[FvW_2(CO)_6{}^{2-}]$[10a] and other

models.[10b] Thus, the effect of the charge on the remainder of the molecule seems

minimal.
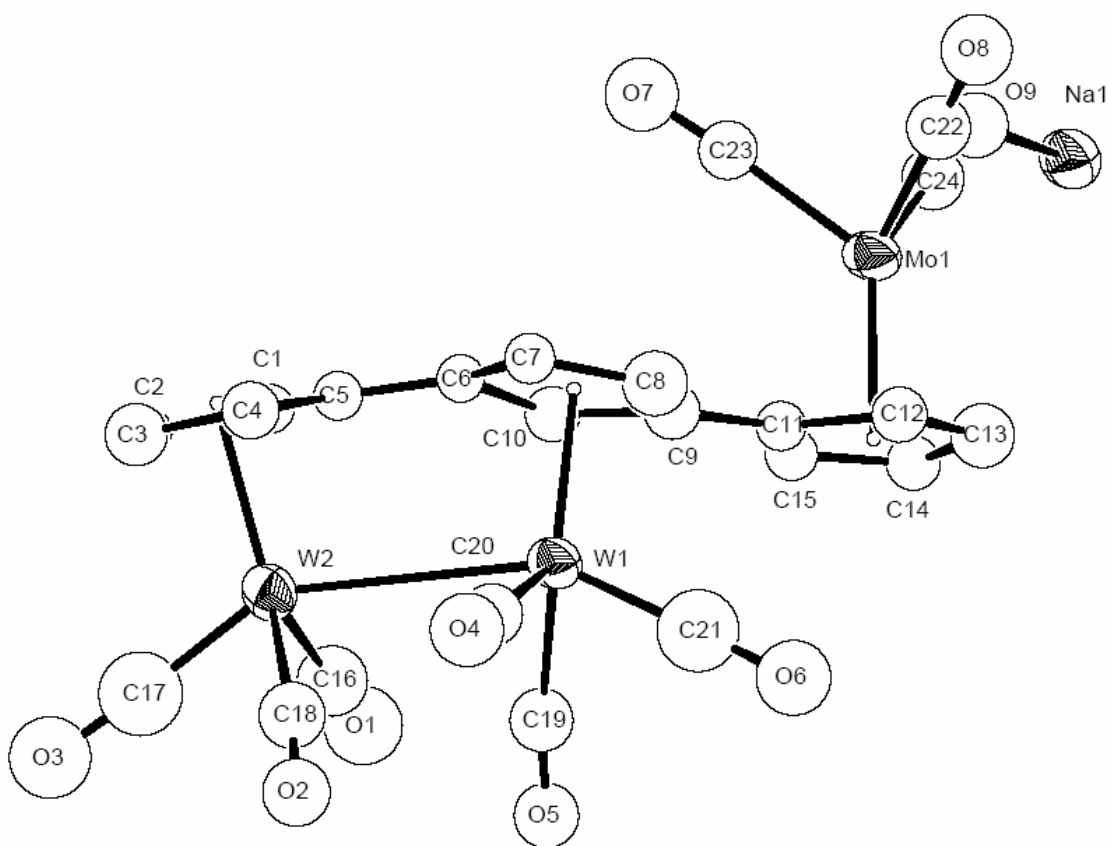

Figure 1. Averaged structure of **3-Na$^+$•(THF)$_5$** in the crystal (from THF-pentane by

diffusion), modeled as a 65:35 mixture of **A:B**. The metal labeling is arbitrarily that of

the major form. The solvating THF molecules, of which four are ligating Na$^+$, are omitted

for clarity. Selected distances [Å] and angles [˚] (cf. reference 3b): W1–W2 3.268(2),

C5–C6 1.37(5), C9–C11 1.42(3), W1–Cp (centroid) 2.003, W2–Cp 2.165, Mo1–Cp

2.065; C4–C5–C6–C10 152(2), C1–C5–C6–C7 175(2).

___We find that the systems investigated are in equilibrium between the two forms **A** and

B, directly observable as such for **1-6** and **11**, and/or approachable from one or both sides

for **9**, **10**, and **12** (Table 2). VT NMR experiments with the anions **1-4** revealed line

broadening on warming, but, because of the onset of decomposition >80 ˚C, the

complexity of the spectra, and the required exacting kinetic modeling, only **2** was

quantified in this manner (Table 2). In as much as it is representative of the structurally

very similar anion series, the small $\Delta S^{\ddagger}$ value suggests little overall additional order in the

transition state of the exchange. In conjunction with a clean first order rate law and

concentration independent rate, these data point to a strictly intramolecular process.

Kinetic data suitable for comparison within the series and with the rates reported for the

intermolecular variants[2, 11] were readily accessible for **1-4** by EXSY spectroscopy (Table

2), showing chemical exchange between six pairs of hydrogens, e.g., H2/H11, H3/H10,

etc. (Scheme 1).[12] These rates for **1** and **2** are solvent polarity independent (CH$_3$CN,

CH$_2$Cl$_2$, THF) and are unchanged (**1**) on adding up to a tenfold excess of NaBF$_4$ or using

the pure Na$^+$ salt. The effective molarity k_{intra}/ k_{inter} [11, 13] for the exchanges in **1** and **4** is

~10^5 and ~10^4, respectively, consistent with their intramolecular nature. It also shows the

absence of any unusual kinetic effects that might have been precipitated by the geometry

of the systems.[14]

___The two extreme mechanistic possibilities for these electron transfer processes are nucleophilic substitution (either concerted or associative, perhaps with central Cp-ring slippage) and outer sphere single electron transfer.[1, 2] The latter would generate a dinuclear radical anion moiety,[15] which could equilibrate via an all-non-metal-metal-bonded diradical anion[15c] or by the direct S_{RN} displacement shown in Scheme 2. A distinction between these options is often difficult.[1, 2, 16] Table 2 reveals a progressive rate decrease on going from **1** to **4**, incongruent with S_N2, considering the greater nucleophilicity of [CpW(CO)$_3^-$] relative to [CpMo(CO)$_3^-$] in methylations. The latter also show measurable effects of solvent polarity and the nature of the counter ion, absent in our systems.[17] Particularly relevant are cases in which the leaving group is the same, i.e.
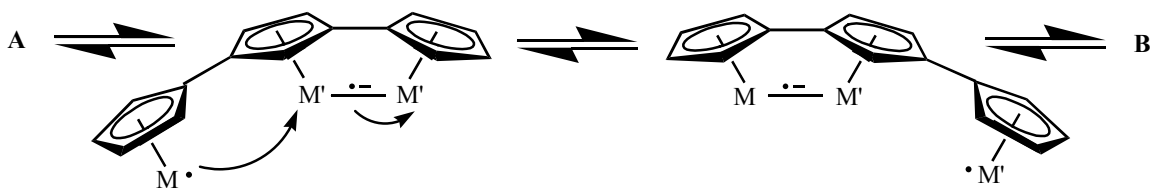
Scheme 2. Electron transfer mechanism of anions **1-4**.

$k_1/k_{2f} = 1.25$ and $k_{3f}/k_4 = 1.57$, data that speak against direct nucleophilic displacement. An associative mechanism with concurrent ring slippage[18] remains an option, however.[2a, c] SET appears most attractive, in particular because the trends in Table 2 follow those expected on the basis of redox potentials.[15b] Subsequent metal–metal bond homolysis to an intermediate diradical anion (equivalent to metal–metal bond homolysis in the starting anion) seems energetically unattractive, considering our activation parameters (Table 2), hence, we suggest the mechanism depicted in Scheme 2.

6

___The equilibrium data highlight the advantages of intramolecular exchange in **1 - 4** in the estimation of (relative) bond strengths, because structural, solvation, and entropy effects, and the imponderables of electrochemical measurements[19] should effectively cancel. For this purpose, we relate thermochemically the anions to their corresponding radicals. Specifically, the difference ΔH^o in metal–metal bond dissociation energies (BDE) in solution in going from **A** to **B** can be estimated from K (hence ΔG^o) of the anion equilibrium and the difference in the known oxidation potentials of the anionic fragments by Eq. (1).[19]

$$\Delta H^o = -1.36\log K - 23.1[E_{ox}(M^-) - E_{ox}(M'^-)] \text{ kcal mol}^{-1} \text{ (all in CH}_3\text{CN, 300 K)} \qquad (1)$$

The results (Table 2) indicate a W–W bond that is only ~ 2 kcal mol^{-1} stronger than Mo–Mo, the mixed metal bond energy lying in between, as expected.[20] Turning to the literature on [CpM(CO)$_3$]$_2$, the measured Mo–Mo BDE (32.5 kcal mol^{-1})[21a] appears reliable,[15a] however, that for W–W (56.0 kcal mol^{-1})[21b] has been queried repeatedly as being too high.[3c, 19c, 21c] Adopting the reasonable assumption that Fv intermetallic bonds are enthalpically equivalent to those in Cp dimers, certainly for lower triad metals,[22] we suggest 34.5 kcal mol^{-1}. Several control experiments support the validity of this approach. Thus, the ΔH^o values for **5** and **6** [Eq.(2)] are exactly as expected, therefore negating the significance of any untoward anion effects (vide supra).

$$\Delta H^o = -1.36\log K - (\text{BDE}_{MH} - \text{BDE}_{M'H}) \qquad (2)$$

For example, and to illustrate our procedure, for **5**: BDE_{WH} = 72.4 kcal mol^{-1},[19a, c]

BDE_{MoH} = 69.3 kcal mol^{-1}[19a, c], BDE_{MoMo} = 32.5 kcal mol^{-1},[21a] BDE_{WMo} = 33.5 kcal

mol^{-1} (vide supra); hence, the isomerization **5a** to **5b** should be endothermic by +2.1 kcal

mol^{-1}, providing a K = 0.03, as observed. Similarly, the topological intermolecular

equivalents of the equilibrations of **2** and **3**, namely [FvMoW(CO)$_6^{2-}$] + [FvMo$_2$(CO)$_6$]

(K = 2.3) or + [FvW$_2$(CO)$_6$] (K = 0.3) conform with the values in Table 2 for **2** and **3**.

They are also internally consistent ([FvW$_2$(CO)$_6^{2-}$] + [FvMo$_2$(CO)$_6$], K = 4; expected: 2.3

x (1/0.3) = 7.6). The other entries in Table 2 serve to highlight the utility of the

framework in confirming or questioning literature data. For example, for the equilibrium

of **7**, the measured $K \leq 0.01$ provides $\Delta G^o \geq$ +2.7 kcal mol^{-1}. With [$E_{ox}(Cr^-) - E_{ox}(Mo^-)$]

= –0.688 –(–0.385) V = –0.303 V,[19a, c] one can derive a minimum estimate of how

much weaker Mo–Cr is relative to Mo–Mo: $\geq$9.7 kcal mol^{-1}. This appears reasonable,

since, using BDE(Mo–Mo) = 32.5 kcal mol^{-1} [21a] and BDE(Cr–Cr) 14.7 kcal mol^{-1},[22]

one would expect BDE(Cr–Mo) to be about 23.6 kcal mol^{-1} (the mean), i.e. a ΔH^o (Table

2) of 8.9 kcal mol^{-1}. A similar estimate for **8**, applying the new W–W number from

above, furnishes 9.9 (found: $\geq$9.8) kcal mol^{-1}. Lesser agreement is evident in the Ru

complexes. Because the equilibria of **9** and **12** lie in the direction dictated by the

difference in E_{ox} values[19a, c] and metal–CH$_3$ energies[23b, c], respectively, a meaningful

estimation of their associated ΔH^o values is not possible. However, those of **10** and, even

better, **11**, imply a Ru–Mo BDE of more than 7 kcal mol^{-1} less than that of Mo–Mo and,

correspondingly, a Ru–W bond 7.8 kcal mol^{-1} weaker than that in W–W. These numbers

would suggest Ru–Ru BDEs of < 20 kcal mol^{-1}, incompatibly low with other estimates

and qualitative observations.[5b] The culprit may be a deficiently low Ru–H BDE (or,

rather, a too negative $E_{ox}(Ru^-)$.[19] Such is indeed indicated by gas phase trends

[BDE(Ru–H)] > (Mo–H)],[23a] M–alkyl BDEs as they pertain to analog **12** (i.e.

BDE[CpMo(CO)$_3$–CH$_3$] < BDE[CpRu(CO)$_3$–CH$_3$]),[23b, c] and the correspondence

between hydride and alkylmetal bond strengths.[23a, e]

___To close, we have demonstrated the unique utility of the terCp ligand as a platform on

which to carry out otherwise intractable kinetic and thermodynamic measurements of

intramolecular electron (and ligand) exchange reactions along a trimetallic array. Future

work is directed toward manipulation of the ligand (e.g. a central indenyl fragment, to

further probe potential ring slippage) and the trimetallic array (e.g. rendition of an M–

M'–M sequence for consonance with Marcus theory) for mechanistic purposes, and the

juxtaposition of metal pairs judiciously chosen (e.g. 0<K<1) to allow for the

determination of their relative intermetallic bond strengths, a task of general importance

in catalysis and mechanistic investigations.

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[8] For example, for **1-Na$^+$**, the IR spectrum (Table 1) is a composite of that of FvMo$_2$(CO)$_6$ ($\tilde{v}$ = 2010, 1960, 1925, 1905 cm^{-1}) and ion-paired CpMo(CO)$_3^-$Na$^+$ ($\tilde{v}$ = 1899, 1796, 1743 cm^{-1}), whereas for **1-Bu$_4$N$^+$** the two low energy bands merge to a single peak at 1792 cm^{-1}.

[9] Confirmed by dissolution of the crystals at −78 ˚C and NMR analysis. Crystal size 0.13 x 0.11 x 0.04 mm^3, space group $P2_1$ (no. 4), scan range 3.00<2θ<46.2˚, a = 10.7286(9), b = 14.910(1), c = 14.922(1), β = 102.659(2) Å, V = 2328.9(3) Å^3, Z = 2, ρ_{calcd} = 1.84 g cm^{-3}, μ(Mo$_{K\alpha}$) = 52.70 cm^{-1}, 6944 unique reflections at −97 ˚C, of which 3207 were taken as observed [F_o>3.00σ(F_o)], R = 0.064, R_w = 0.058. CCDC-215769 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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<TAB> Table 1. Complete or representative physical data of **1-12**.[4]

1-Na$^+$: red needles (from THF/hexanes); m.p. 107-110 ˚C (decomp); ^{1}H NMR (400 MHz, CD$_3$CN; numbering as in A in Scheme 1): δ = 5.71 (m, 2H, H5, H6), 5.41 (m, 1H, H10), 5. 38 (m, 1H, H9), 5.30 (m, 1H, H2), 5.08 (m, 1H, H4), 5.02 (m, 1H, H3), 4.80 (t, J = 1.8 Hz, 1H, H1), 4.44 (m, 1H, H8), 4.39 (m, 1H, H7), 4.37 (m, 1H, H11). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ = 235.7 (Mo–CO), 110.2, 96.3, 95.6, 93.2, 87.7, 87.66, 87.60 (2C), 86.7, 86.6, 85.0 (2C), 84.6, 83.7, 80.2; IR (THF): $\tilde{\nu}$ = 2011 (s), 1960 (s br), 1926 (s br), 1902 (s br), 1804 (m br), 1756 (m br) cm^{-1}; MS (electrospray): m/z (%): 731 ([M^-], 100), 703 (50), 673 (48).

2-Na$^+$: ^{1}H NMR (300 MHz, CD$_3$CN): (isomer **A**) δ = 5.65 (m, 1H, H6), 5.63 (m, 1H, H5), 5.38 (m, 2H, H9, H10), 5.26 (m, 1H, H2), 5.03 (m, 1H, H4), 4.98 (m, 1H, H3), 4.88 (t, J = 1.6 Hz, 1H, H1), 4.49 (m, 1H, H7), 4.46 (m, 2H, H8, H11); (isomer **B**; numbering as in topology **A** of Scheme 1) δ 5.63 (m, 2H, H5, H6), 5.38 (m, 2H, H9, H10), 5.31 (m, 1H, H2), 5.03 (m, 1H, H4), 4.98 (m, 1H, H3), 4.97 (t, J = 1.6 Hz, 1H, H1), 4.68 (m, 1H, H8), 4.65 (m, 1H, H11), 4.55 (dd, J = 1.6, 1.1 Hz, 1H, H7); IR (THF): $\tilde{\nu}$ = 2010 (s), 1959 (s br), 1925 (s br), 1901 (s), 1802 (w), 1755 (w) cm^{-1}.

3-Na$^+$•(THF)$_5$: dark red needles (from THF/pentane); m.p. 97 - 99 ˚C (decomp); ^{1}H NMR (300 MHz, CD$_3$CN): (isomer **A**) δ = 5.66 (m, 1H, H6), 5.63 (m, 1H, H5), 5.40 (m, 1H, H10), 5.36 (m, 1H, H9), 5.33 (m, 1H, H2), 5.08 (m, 1H, H4), 5.07 (m, 1H, H1), 5.03 (m, 1H, H3), 4.74 (m, 1H, H8), 4.66 (m, 1H, H11), 4.65 (m, 1H, H7); (isomer **B**) δ = 5.69 (m, 1H, H6), 5.64 (m, 1H, H5), 5.40 (m, 1H, H10), 5.36 (m, 1H, H9), 5.28 (m, 1H, H2),

5.08 (m, 1H, H4), 5.03 (m, 1H, H3), 4.97 (t, J = 1.9 Hz, 1H, H1), 4.58 (m, 1H, H7), 4.53 (m, 1H, H8), 4.48 (m, 1H, H11); IR (THF): $\tilde{\nu}$ = 2008(s), 2009 (s), 1958 (vs), 1922 (s br), 1900 (m), 1799 (w), 1758 (w) cm^{-1}; MS (electrospray): m/z (%): 907 (M^-).

4-Na$^+$: ^{1}H NMR (300 MHz, CD$_3$CN): δ = 5.66 (m, 1H, H6), 5.61 (m, 1H, H5), 5.40 (m, 1H, 10), 5.38 (m, 1H, H9), 5.30 (m, 1H, H2), 5.09 (m, 2H, H1, H4), 5.05 (m, 1H, H3), 4.74 (m, 1H, H8), 4.68 (m, 1H, H11), 4.65 (m, 1H, H7); IR (THF): $\tilde{\nu}$ = 2008 (s), 1956 (s), 1921 (m), 1897 (m), 1799 (w), 1750 (w) cm^{-1}.

5A, **B**: ^{1}H NMR (300 MHz, CD$_3$CN, hydride signals): δ = –2.4 (s, 0.03H), –6.97 [s, 1H, $J(^{183}$W-^{1}H) = 38 Hz].

6A, **B**: ^{1}H NMR (300 MHz, CD$_3$CN, hydride signals): δ = –2.2 (s, 0.03H), –6.90 [s, 1H, $J(^{183}$W-^{1}H) = 38 Hz].

7: ^{1}H NMR (300 MHz, CD$_3$CN): δ = 5.63 (dd, J = 1.8, 2.6 Hz, 1H, H6), 5.38 (m, 2H, H9, H10), 5.00 (m, 1H, H5), 4.75 (t, J = 1.6 Hz, 1H, H1), 4.60 (m, 1H, H2), 4.43 (m, 4H, H3, H4, H8, H11), 4.39 (m, 1H, H7); IR (THF): $\tilde{\nu}$ = 2010 (s), 1962 (s), 1925 (s), 1899 (sh), 1794 (w), 1754 (w) cm^{-1}.

8-Na$^+$ (isomer **A**): dark red needles (from THF/pentane); m.p. 103 - 105 ˚C (decomp); ^{1}H NMR (300 MHz, CD$_3$CN): δ = 5.62 (dd, 1H, J = 3.0, 1.8 Hz, H6), 5.40 (m, 1H, H10), 5.36 (m, 1H, H9), 5.03 (t, J = 1.8 Hz, 1H, H1), 4.97 (m, 1H, H5), 4.74 (m, 1H, H8), 4.66

(m, 3H, H2, H7, H11), 4.47 (m, 1H, H4), 4.43 (m, 1H, H3); $^{13}C\{^1H\}$ NMR (100 MHz, CD$_3$CN, quaternary and W–CO carbons not observed): δ = 245 (Cr–CO), 89.8, 85.5, 85.5, 83.5, 83.5, 83.4, 82.7, 82.2, 82.0, 81.9, 78.9; IR (THF): $\tilde{v}$ = 2008(s), 1955 (vs), 1920 (vs br), 1898 (m), 1803 (w), 1756 (w) cm^{-1}; MS (electrospray): m/z (%): 859 ([M^-], 5), 727 (100).

9-Et$_4$N$^+$ (isomer A): yellow powder (from hexane-acetone); m.p. >300 ˚C (decomp); ^1H NMR (500 MHz, CD$_3$CN): δ = 6.03 (dd, J = 2.8, 1.7 Hz, 1H, H6), 5.79 (ddd, J = 2.8, 2.8, 1.6 Hz, 1H, H9 or H10), 5.74 (ddd, J = 2.8, 2.8, 1.6 Hz, 1H, H9 or H10), 5.70 (ddd, J = 3.1, 1.8, 1.8 Hz, 1H, H5), 5.31 (ddd, J = 3.0, 1.9, 1.9 Hz, 1H, H2), 5.06 (ddd, J = 2.9, 2.9, 1.8 Hz, 1H, H3 or H4), 5.03 (ddd, J = 2.9, 2.9, 1.8 Hz, 1H, H3 or H4), 4.53 (dd, J = 1.9, 1.9 Hz, 1H, H1), 4.21 (m, 1H, H8), 4.00 (m, 2H, H7, H11), 3.15 (q, J = 7.2 Hz, 8H), 1.19 (tt, J = 7.2, 1.8 Hz, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, CD$_3$CN): δ = 235.9, 208.4, 207.4, 207.3, 206.8, 111.8, 97.3, 94.8, 92.5, 89.6, 89.5, 87.8, 87.4, 87.2, 87.0, 85.5, 79.9, 79.6, 78.2, 76.1, 53.0 (t, J = 3.9 Hz), 7.60; IR (CH$_3$CN): $\tilde{v}$ = 2008, 1947, 1902, 1786, 1738 cm^{-1}; FAB-MS (18-crown-6): m/z: 685 (M^-); (isomer B): ^1H NMR (300 MHz, CD$_3$CN, –70 ˚C): δ = 6.06 (s, 1H), 5.46 (s, 1H), 5.38 (s, 1H), 5.00 (m, 3H), 4.76 (s, 2H), 4.59 (s, 2H), 4.22 (s, 1H).

10 (isomer A): ^1H NMR (400 MHz, THF-d_8): δ = 6.22 (m, 2H), 5.84 (m, 1H), 5.82 (m, 2H), 5.59 (m, 1H), 5.53 (m, 1H), 4.74 (dd, J = 1.8, 1.8 Hz, 1H), 4.25 (m, 3H), −5.25 (s, 1H); (isomer B): yellow orange crystals (from hexane-acetone); m.p. 188-189 ˚C (decomp); ^1H NMR (400 MHz, THF-d_8): δ = 6.22 (dd, J = 2.9, 1.7 Hz, 1H), 6.10 (ddd, J

= 2.9, 1.7, 1.7 Hz, 1H), 5.72 (ddd, J = 2.9, 1.7, 1.7 Hz, 1H), 5.47 (ddd, J = 2.8, 2.8, 1.7 Hz, 1H), 5.45 (m, 2H), 5.42 (ddd, J = 2.8, 2.8, 1.7 Hz, 1H), 4.77 (dd, J = 1.8, 1.8 Hz, 1H), 4.65 (ddd, J = 3.2, 1.6, 1.6 Hz, 1H), 4.64 (ddd, J = 3.2, 1.6, 1.6 Hz, 1H), 4.25 (dd, J = 2.9, 1.9 Hz, 1H), −10.89 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8, −65 ºC): δ = 236.2, 224.0, 223.6, 206.2, 205.5, 202.03, 202.00, 103.1, 99.3, 98.3, 90.9, 88.1, 88.0, 86.9, 86.4, 86.3, 86.2 (2C), 85.3, 85.1, 76.6, 74.3; IR (THF): $\tilde{v}$ = 2025, 1969, 1907, 1891 cm^{-1}; FAB-MS (sulfolane): m/z: 685 (M^+).

11 (isomer **A**): ^{1}H NMR (400 MHz, THF-d_8): δ = 6.29 (ddd, J = 2.9, 1.8, 1.8 Hz, 1H), 6.25 (dd, J = 2.9, 1.8 Hz, 1H), 5.87 (m, 1H), 5.84 (m, 1H), 5.81 (m, 1H), 5.67 (ddd, J = 2.9, 2.9, 1.8 Hz, 1H), 5.61 (ddd, J = 2.9, 2.9, 1.8 Hz, 1H), 4.75 (dd, J = 1.8, 1.8 Hz, 1H), 4.29 (m, 3H), −6.92 (s, J(^{183}W-H) = 37.4 Hz, 1H); (isomer **B**): δ = 6.24 (dd, J = 2.8, 1.7 Hz, 1H), 6.09 (m, 1H), 5.72 (m, 1H), 5.47 (ddd, J = 2.8, 2.8, 1.7 Hz, 1H), 5.43 (m, 3H), 4.86 (dd, J = 1.8, 1.8 Hz, 1H), 4.82 (m, 2H), 4.34 (dd, J = 2.9, 2.0 Hz, 1H), −10.88 (s, 1H).

12 (isomer **A**):[a] ^{1}H NMR (300 MHz, THF-d_8): δ = 6.21 (dd, J = 2.9, 1.8 Hz, 1H), 5.97 (ddd, J = 2.8, 1.8, 1.8 Hz, 1H), 5.85 (m, 2H), 5.55 (ddd, J = 2.8, 1.8, 1.8 Hz, 1H), 5.48 (ddd, J = 2.8, 2.8, 1.8 Hz, 1H), 5.39 (ddd, J = 2.8, 2.8, 1.8 Hz, 1H), 4.71 (dd, J = 1.8, 1.8 Hz, 1H), 4.31 (m, 3H), 0.35 (s, 3H); (isomer **B**): ^{1}H NMR (400 MHz, THF-d_8): δ = 6.16 (dd, J = 2.8, 1.8 Hz, 1H), 5.88 (m, 1H), 5.51 (m, 1H), 5.49 (m, 1H), 5.45 (m, 3H), 4.71 (dd, J = 1.8, 1.8 Hz, 1H), 4.64 (m, 2H), 4.28 (m, 1H), 0.36 (s, 3H).

[a] Ref. [3b].

<TAB> Table 2. Kinetic and/or equilibrium data for **1-12**, **A** → **B**, at 300 K in CH_3CN.

Compound[1]	k (Hz)	K_{eq}	$\Delta H^{o[a]}$ (kcal mol^{-1})	Compound	K_{eq}	$\Delta H^{o[a]}$ (kcal mol^{-1})
1[b]	3.0	1.0		**6**[c]	30	1.0
2[b]	2.4 (k_f)	2.26[d]	−0.62	**7**	≤ 0.01[e]	≥9.7
	1.1 (k_r)			**8**	≤ 0.01[e]	≥9.8
3[b]	0.11 (k_f)[f]	0.32	0.81	**9**[g]	≤ 0.01	[h]
	0.36 (k_r)[f]			**10**[c, i]	≥100[e]	≤−7.0
4[b]	0.07[f]	1.0		**11**[c, j]	2	−7.8
5[c]		0.03	−1.0	**12**[k]	≥100[e]	[h]

[a] Estimate of $\Delta BDE_{(M'-M')-(M-M')}$; see text. We use the (corrected) E_{ox} values (V) from Table I, ref.[19c], Cr −0.688 , Mo −0.385 , W −0.379 , Ru −0.941, and metal hydride BDEs (kcal mol^{-1}) from ref. [19a], Mo–H 69.3, W–H 72.4, Ru–H 65.0. [b] Bu_4N^+ salts. NMR data and K values are unchanged from those of the Na^+ salts. [c] Equilibration is accelerated by added pyridine, retarded by added acetic acid. [d] In addition, complementary VT NMR analysis and theoretical fit of the coalescence of the signals for H1 (δ = 4.88, **A**, and 4.97 ppm, **B**, furnishes $\Delta H^{\ddagger}$ = 16.2 (±2.4) kcal mol^{-1} and $\Delta S^{\ddagger}$ = −3.5 (±7) e.u. [e] ΔG^o ≤ − 2.7 kcal mol^{-1} (for K_{eq} ≤ 0.01) or ≥ + 2.7 kcal mol^{-1} (for K_{eq} ≥100). [f] Extrapolated from measurements at 313 (**3**) and 323 K (**4**). [g] Equilibrium established by deprotonation of either of the two hydrides **10A** and **B.** [h] Bracketing not meaningful. [i] Established by conversion of **10A** to **B** in THF. [j] Established by conversion of **11A** to **11B**. [k] Established by very slow (weeks), but clean, complete conversion of **12A** to **B** (see ref. [23d]).

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The metallomeric equilibrium between **A** and **B** can be observed and quantified kinetically and thermodynamically by direct NMR techniques, providing insights into the mechanism of a fundamental organometallic displacement reaction and allowing for the estimation of relative metal–metal bond strengths in cyclopentadienylmetals.

$$K = k_f/k_r$$

A   **B**