Transition-Metal Complexes

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

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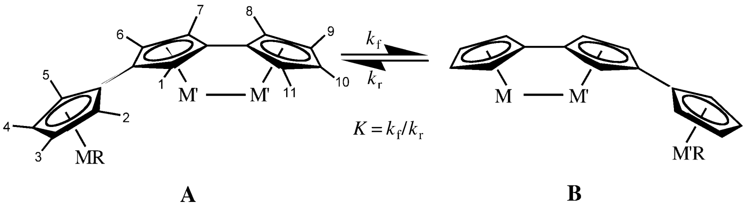
Electron transfer is fundamental to chemical reactivity.[1] A prototype example in organometallic chemistry is the attack of an anionic metal center on a metal–metal bond ($M^- + M'{-}M'$), which by nucleophilic substitution should lead to $M{-}M' + M'^-$. Such a result is not cleanly found, however,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



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.

The required materials were made according to described protocols (see Experimental Section),[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**) *t*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 attached fulvalene (Fv) nuclei,[5] via the characteristic three- (≈ 3 Hz) and four-bond (≈ 1.7 Hz) couplings in ligating cyclopentadienyls (Cps),[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. 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$^{(\prime)}$ and CpM$^{(\prime)}$ 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 forms 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, for example, **1**–**4** (R = CH$_3$), and **12**. In particular, the hydrogen atoms 1 and 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 ($P2_1$, 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 ratio of the two isomers **A** and **B** and was successfully modeled as such.[9] The structural details for the FvM–M$^{(\prime)}$ 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 unit resembles (for example, with respect to

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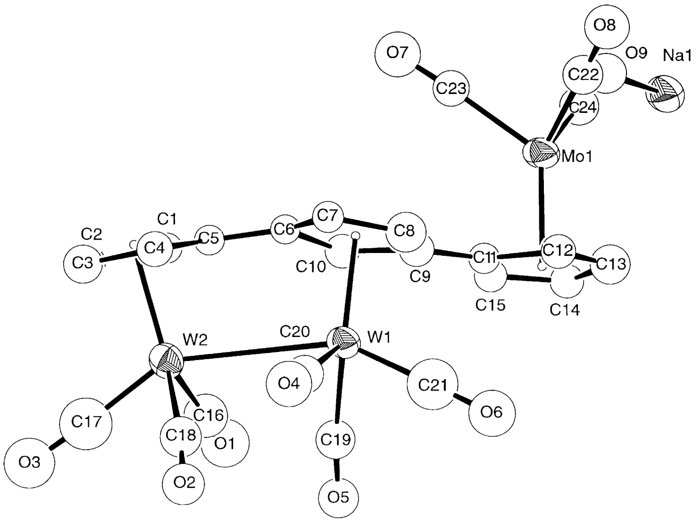
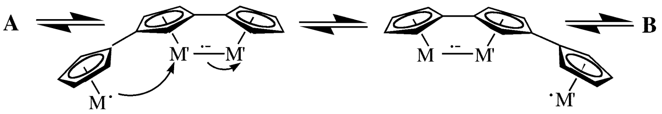


Figure 1. Averaged structure of **3**-Na$^+$·(THF)$_5$ in the crystal (from THF/pentane by diffusion), modeled as a 65:35 mixture of **A**:**B**. The metal labeling is arbitrarily that of the major form. The solvating THF molecules, of which four are ligating Na$^+$ ions, are omitted for clarity. Selected distances [Å] and angles [°] (compare with ref. [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).

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.

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 1). Variable-temperature NMR experiments with the anions **1**–**4** revealed line broadening on warming, but because of the onset of decomposition at >80 °C, the complexity of the spectra, and the required exacting kinetic modeling, only **2** was quantified in this manner (Table 1). 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 1), which show chemical exchange between six pairs of hydrogen atoms (e.g., H2/H11, H3/H10; Scheme 1).[12] The rates for **1** and **2** are independent of solvent polarity (CH_3CN, CH_2Cl_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 $\approx 10^5$ and $\approx 10^4$, 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 (SET).[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 1 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 counterion, absent in our systems.[17] Particularly relevant are cases in which the leaving group is the same (i.e., $k_1/k_{2f} = 1.25$ 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 1 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 1), hence we suggest the mechanism depicted in Scheme 2.



Scheme 2. Electron-transfer mechanism of anions **1**–**4**.

Table 1: Kinetic and/or equilibrium data for **1**–**12**, **A**→**B**, at 300 K in CH_3CN.

Compound	k [Hz]	K_{eq}	$\Delta H°$ [kcal mol^{-1}][a]	Compound	K_{eq}	$\Delta H°$ [kcal mol^{-1}][a]
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 in 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 ($\delta = 4.88$, **A**, and 4.97 ppm, **B**) furnishes $\Delta H^{\ddagger} = 16.2(\pm 2.4)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -3.5(\pm 7)$ e.u. [e] $\Delta G° = +2.7$ 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]).

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° in metal–metal bond dissociation energies (BDEs) in solution in going from **A** to **B** can be estimated from K (hence ΔG°) of the anion equilibrium and the difference in the known oxidation potentials of the anionic fragments by Equation (1).[19]

$$\Delta H^{o} = -1.36\log K - 23.1[E_{\mathrm{ox}}(\mathrm{M}^-) - E_{\mathrm{ox}}(\mathrm{M'}^-)]\ \mathrm{kcal\,mol^{-1}} \qquad (1)$$

(all in CH_3CN at 300 K)

The results (Table 1) indicate a W–W bond that is only ≈2 kcal mol^{-1} stronger than a Mo–Mo bond, with 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° values for **5** and **6** [Eq. (2)] are exactly as expected, therefore negating the significance of any untoward anion effects.

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

For example, and to illustrate our procedure, for **5**: $\mathrm{BDE_{WH}} = 72.4$ kcal mol^{-1},[19a,c] $\mathrm{BDE_{MoH}} = 69.3$ kcal mol^{-1},[19a,c] $\mathrm{BDE_{MoMo}} = 32.5$ kcal mol^{-1},[21a] $\mathrm{BDE_{WMo}} = 33.5$ kcal mol^{-1}; hence, the isomerization **5a** to **5b** should be endothermic by +2.1 kcal mol^{-1}, providing a value of K of 0.03, as is 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 $[FvMoW(CO)_6]^{2-}$ + $[FvW_2(CO)_6]$ ($K = 0.3$) conform with the values in Table 1 for **2** and **3**. They are also internally consistent ($[FvW_2(CO)_6]^{2-}$ + $[FvMo_2(CO)_6]$, $K = 4$; expected: $2.3 \times (1/0.3) = 7.6$). The other entries in Table 1 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 $\Delta G^\circ \geq +2.7$ kcal mol^{-1}. With $[E_{\mathrm{ox}}(\mathrm{Cr}^-) - E_{\mathrm{ox}}(\mathrm{Mo}^-)] = -0.688 - (-0.385)\ \mathrm{V} = -0.303\ \mathrm{V}$,[19a,c] one can derive a minimum estimate of 9.7 kcal mol^{-1} for how much weaker the Mo–Cr bond is relative to the Mo–Mo bond. 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), that is, a value of ΔH° (Table 1) of 8.9 kcal mol^{-1}. A similar estimate for **8**, applying the new value for the W–W bond given above gives a value for ΔH° of 9.9 (found: ≥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° 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}, which are incompatibly low with other estimates and qualitative observations.[5b] The culprit may be a deficiently low Ru–H BDE (or, rather, a too negative value for $E_{\mathrm{ox}}(\mathrm{Ru}^-)$).[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. $\mathrm{BDE}[CpMo(CO)_3{-}CH_3] < \mathrm{BDE}[CpRu(CO)_3{-}CH_3]$),[23b,c] and the correspondence between hydride and alkylmetal bond strengths.[23a,e]

In summary, 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.

Experimental Section

1-Na$^+$: red needles (from THF/hexanes); m.p. 107–110 °C (decomp); ^{1}H NMR (400 MHz, CD_3CN; numbering as in A in Scheme 1): $\delta = 5.71$ (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 ppm (m, 1H, H11). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN): $\delta = 235.7$ (Mo-*C*O), 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 ppm; IR (THF): $\tilde{\nu} = 2011$ (s), 1960 (s br), 1926 (s br), 1902 (s br), 1804 (m br), 1756 cm^{-1} (m br); MS (electrospray): m/z (%): 731 ([M^-], 100), 703 (50), 673 (48).

2-Na$^+$: ^{1}H NMR (300 MHz, CD_3CN): (isomer **A**) $\delta = 5.65$ (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 ppm (m, 2H, H8, H11); (isomer **B**; numbering as in topology **A** of Scheme 1) $\delta = 5.63$ (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 ppm (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 cm^{-1} (w).

3-Na$^+$·(THF)$_5$: dark red needles (from THF/pentane); m.p. 97–99 °C (decomp); ^{1}H NMR (300 MHz, CD_3CN): (isomer **A**) $\delta = 5.66$ (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 ppm (m, 1H, H7); (isomer **B**) $\delta = 5.69$ (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 ppm (m, 1H, H11); IR (THF): $\tilde{\nu} = 2009$ (s), 2008(s), 1958 (vs), 1922 (s br), 1900 (m), 1799 (w), 1758 cm^{-1} (w); MS (electrospray): m/z (%): 907 ([M^-], 100).

4-Na$^+$: ^{1}H NMR (300 MHz, CD_3CN): $\delta = 5.66$ (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 ppm (m, 1H, H7); IR (THF): $\tilde{\nu} = 2008$ (s), 1956 (s), 1921 (m), 1897 (m), 1799 (w), 1750 cm^{-1} (w).

5 A, **B**: ^{1}H NMR (300 MHz, CD_3CN, hydride signals): $\delta = -2.4$ (s, 0.03 H), -6.97 ppm (s, 1 H, $J(^{183}W\text{-}^{1}H) = 38$ Hz).

6 A, **B**: ^{1}H NMR (300 MHz, CD_3CN, hydride signals): $\delta = -2.2$ (s, 0.03 H), -6.90 ppm (s, 1 H, $J(^{183}W\text{-}^{1}H) = 38$ Hz).

7: ^{1}H NMR (300 MHz, CD_3CN): $\delta = 5.63$ (dd, $J = 1.8$, 2.6 Hz, 1 H, H6), 5.38 (m, 2 H, H9, H10), 5.00 (m, 1 H, H5), 4.75 (t, $J = 1.6$ Hz, 1 H, H1), 4.60 (m, 1 H, H2), 4.43 (m, 4 H, H3, H4, H8, H11), 4.39 ppm (m, 1 H, H7); IR (THF): $\tilde{\nu} = 2010$ (s), 1962 (s), 1925 (s), 1899 (sh), 1794 (w), 1754 cm^{-1} (w).

8-Na^+ (isomer **A**): dark red needles (from THF/pentane); m.p. 103–105 °C (decomp); ^{1}H NMR (300 MHz, CD_3CN): $\delta = 5.62$ (dd, 1 H, $J = 3.0$, 1.8 Hz, H6), 5.40 (m, 1 H, H10), 5.36 (m, 1 H, H9), 5.03 (t, $J = 1.8$ Hz, 1 H, H1), 4.97 (m, 1 H, H5), 4.74 (m, 1 H, H8), 4.66 (m, 3 H, H2, H7, H11), 4.47 (m, 1 H, H4), 4.43 ppm (m, 1 H, H3); $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN, quaternary and W-*C*O carbon resonances not observed): $\delta = 245$ (Cr-*C*O), 89.8, 85.5, 85.5, 83.5, 83.5, 83.4, 82.7, 82.2, 82.0, 81.9, 78.9 ppm; IR (THF): $\tilde{\nu} = 2008$(s), 1955 (vs), 1920 (vs br), 1898 (m), 1803 (w), 1756 cm^{-1} (w); MS (electrospray): *m*/*z* (%): 859 ([M^-], 5), 727 (100).

9-Et_4N^+ (isomer **A**): yellow powder (from hexane/acetone); m.p. > 300 °C (decomp); ^{1}H NMR (500 MHz, CD_3CN): $\delta = 6.03$ (dd, $J = 2.8$, 1.7 Hz, 1 H, H6), 5.79 (ddd, $J = 2.8$, 2.8, 1.6 Hz, 1 H, H9 or H10), 5.74 (ddd, $J = 2.8$, 2.8, 1.6 Hz, 1 H, H9 or H10), 5.70 (ddd, $J = 3.1$, 1.8, 1.8 Hz, 1 H, H5), 5.31 (ddd, $J = 3.0$, 1.9, 1.9 Hz, 1 H, H2), 5.06 (ddd, $J = 2.9$, 2.9, 1.8 Hz, 1 H, H3 or H4), 5.03 (ddd, $J = 2.9$, 2.9, 1.8 Hz, 1 H, H3 or H4), 4.53 (dd, $J = 1.9$, 1.9 Hz, 1 H, H1), 4.21 (m, 1 H, H8), 4.00 (m, 2 H, H7, H11), 3.15 (q, $J = 7.2$ Hz, 8 H), 1.19 ppm (tt, $J = 7.2$, 1.8 Hz, 12 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, CD_3CN): $\delta = 235.9$, 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 ppm; IR (CH_3CN): $\tilde{\nu} = 2008$, 1947, 1902, 1786, 1738 cm^{-1}; FAB-MS ([18]crown-6): *m*/*z*: 685 (M^-); (isomer **B**): ^{1}H NMR (300 MHz, CD_3CN, -70 °C): $\delta = 6.06$ (s, 1 H), 5.46 (s, 1 H), 5.38 (s, 1 H), 5.00 (m, 3 H), 4.76 (s, 2 H), 4.59 (s, 2 H), 4.22 ppm (s, 1 H).

10 (isomer **A**): ^{1}H NMR (400 MHz, [D_8]THF): $\delta = 6.22$ (m, 2 H), 5.84 (m, 1 H), 5.82 (m, 2 H), 5.59 (m, 1 H), 5.53 (m, 1 H), 4.74 (dd, $J = 1.8$, 1.8 Hz, 1 H), 4.25 (m, 3 H), -5.25 ppm (s, 1 H); (isomer **B**): yellow-orange crystals (from hexane/acetone); m.p. 188–189 °C (decomp); ^{1}H NMR (400 MHz, [D_8]THF): $\delta = 6.22$ (dd, $J = 2.9$, 1.7 Hz, 1 H), 6.10 (ddd, $J = 2.9$, 1.7, 1.7 Hz, 1 H), 5.72 (ddd, $J = 2.9$, 1.7, 1.7 Hz, 1 H), 5.47 (ddd, $J = 2.8$, 2.8, 1.7 Hz, 1 H), 5.45 (m, 2 H), 5.42 (ddd, $J = 2.8$, 2.8, 1.7 Hz, 1 H), 4.77 (dd, $J = 1.8$, 1.8 Hz, 1 H), 4.65 (ddd, $J = 3.2$, 1.6, 1.6 Hz, 1 H), 4.64 (ddd, $J = 3.2$, 1.6, 1.6 Hz, 1 H), 4.25 (dd, $J = 2.9$, 1.9 Hz, 1 H), -10.89 ppm (s, 1 H); $^{13}C\{^{1}H\}$ NMR (100 MHz, [D_8]THF, -65 °C): $\delta = 236.2$, 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 ppm; IR (THF): $\tilde{\nu} = 2025$, 1969, 1907, 1891 cm^{-1}; FAB-MS (sulfolane): *m*/*z*: 685 (M^+).

11 (isomer **A**): ^{1}H NMR (400 MHz, [D_8]THF): $\delta = 6.29$ (ddd, $J = 2.9$, 1.8, 1.8 Hz, 1 H), 6.25 (dd, $J = 2.9$, 1.8 Hz, 1 H), 5.87 (m, 1 H), 5.84 (m, 1 H), 5.81 (m, 1 H), 5.67 (ddd, $J = 2.9$, 2.9, 1.8 Hz, 1 H), 5.61 (ddd, $J = 2.9$, 2.9, 1.8 Hz, 1 H), 4.75 (dd, $J = 1.8$, 1.8 Hz, 1 H), 4.29 (m, 3 H), -6.92 ppm (s, $J(^{183}W\text{-}H) = 37.4$ Hz, 1 H); (isomer **B**): $\delta = 6.24$ (dd, $J = 2.8$, 1.7 Hz, 1 H), 6.09 (m, 1 H), 5.72 (m, 1 H), 5.47 (ddd, $J = 2.8$, 2.8, 1.7 Hz, 1 H), 5.43 (m, 3 H), 4.86 (dd, $J = 1.8$, 1.8 Hz, 1 H), 4.82 (m, 2 H), 4.34 (dd, $J = 2.9$, 2.0 Hz, 1 H), -10.88 ppm (s, 1 H).

12 (isomer **A**):[3b] ^{1}H NMR (300 MHz, [D_8]THF): $\delta = 6.21$ (dd, $J = 2.9$, 1.8 Hz, 1 H), 5.97 (ddd, $J = 2.8$, 1.8, 1.8 Hz, 1 H), 5.85 (m, 2 H), 5.55 (ddd, $J = 2.8$, 1.8, 1.8 Hz, 1 H), 5.48 (ddd, $J = 2.8$, 2.8, 1.8 Hz, 1 H), 5.39 (ddd, $J = 2.8$, 2.8, 1.8 Hz, 1 H), 4.71 (dd, $J = 1.8$, 1.8 Hz, 1 H), 4.31 (m, 3 H), 0.35 ppm (s, 3 H); (isomer **B**): ^{1}H NMR (400 MHz, [D_8]THF): $\delta = 6.16$ (dd, $J = 2.8$, 1.8 Hz, 1 H), 5.88 (m, 1 H), 5.51 (m, 1 H), 5.49 (m, 1 H), 5.45 (m, 3 H), 4.71 (dd, $J = 1.8$, 1.8 Hz, 1 H), 4.64 (m, 2 H), 4.28 (m, 1 H), 0.36 ppm (s, 3 H).

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[9] Confirmed by dissolution of the crystals at -78 °C and NMR analysis. Crystal size $0.13 \times 0.11 \times 0.04$ mm^3, space group $P2_1$ (no. 4), scan range $3.00 < 2\theta < 46.2°$, $a = 10.7286(9)$, $b = 14.910(1)$, $c = 14.922(1)$ Å, $\beta = 102.659(2)°$, $V = 2328.9(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.84$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 52.70$ cm^{-1}, 6944 unique reflections at -97 °C, of which 3207 were taken as observed [$F_o > 3.00\sigma(F_o)$], $R = 0.064$, $R_w = 0.058$. 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 CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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