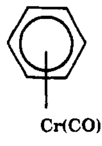
sensitive to small amounts of nucleophilic species such as MeOH, H_2O, MeCN, Me_2CO, and THF. For example, the addition of MeOH or MeCN at <0.1 M completely destroyed the reversibility. The addition of TBAP at only 0.003 M to **1** in CH_2Cl_2 with $TBAPF_6$ at 0.1 M also resulted in the loss of reversibility. It is likely that the enhanced persistence of 1^+ in $TBAPF_6/CH_2Cl_2$ relative to TBAP/CH_2Cl_2 is due to the lower nucleophilicity of PF_6^- compared to ClO_4^- and not due to any special stabilization of 1^+ by PF_6^-. It is possible that simple ion pair formation between 1^+ and PF_6^- serves to protect 1^+ from attack by nucleophiles. By using careful drying procedures, storing all materials in oven-dried containers and performing Karl Fischer titrations, it was established that the observed behavior was not due to water present as an impurity. The effects described above were independent of the electrode material (platinum, gold, glassy carbon), suggesting that adsorption is not playing a significant role. To verify this point, double-potential-step chronocoulometry was performed on a solution of **1** in CH_2Cl_2 (0.1 M $TBAPF_6$) at −30 °C. In these experiments the potential was stepped from +0.35 to +1.1 V and back to +0.35 V. The amount of time (τ) at +1.1 V was varied from 0.050 to 5.0 s. Standard plots[25] of Q_f vs. $t^{1/2}$ ($t < \tau$) and Q_r vs. θ ($t > \tau$; $\theta = \tau^{1/2} - t^{1/2} + (t - \tau)^{1/2}$) as well as plots of Q_f vs. $t^{1/2}$ for solutions containing only electrolyte gave within error identical intercepts for a given electrode (platinum, gold, glassy carbon). This indicates that adsorption is not significant.

In order to quantify the effect of $TBAPF_6$ relative to TBAP, CV's obtained at −30 °C were compared to ones calculated[26] by digital simulation for an EC mechanism. At this temperature the $1^+/1$ couple was partially reversible with TBAP at scan rates above 100 mV/s; with $TBAPF_6$ the couple was completely reversible at all scan rates employed (10 to 1000 mV/s). The best fit of the data with TBAP gave a rate constant (k) for the irreversible decomposition of 1^+ of 1.4 s^{-1}, while in the presence of $TBAPF_6$ $k < 0.005$ s^{-1}. The conclusion is that $TBAPF_6$ reduces the rate of decomposition of 1^+ by at least a factor of 250.

A variety of other π-hydrocarbon complexes (**2**–**6**) were briefly investigated in order to test the utility of LTCV in organometallic chemistry and to test the generality of the $TBAPF_6$ effect noted above. All the complexes **2**–**6** showed cleaner and more reversible CV's at lower temperatures, and with **2**, **3**, and **5** completely irreversible oxidations at room temperature were converted to reversible ones at low temperatures. With **3**, **5**, and **6** the use of $TBAPF_6$ instead of TBAP was investigated with $TBAPF_6$ giving much more reversible behavior in each case.

In conclusion, we have shown that LTCV in dichloromethane can be a useful technique in organometallic chemistry and that the use of $TBAPF_6$ instead of TBAP or other supporting electrolytes may give significantly more persistent radicals in electrochemical oxidations.

Acknowledgment. This work was supported by the National Science Foundation (CHE-8521189) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We are grateful to T. J. Alavosus, Y. K. Chung, and C. A. Camaioni-Neto for providing some of the complexes and to D. K. Gosser and P. H. Rieger for the use of the digital simulation program and for helpful discussions.



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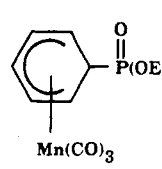

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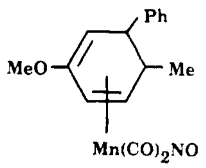

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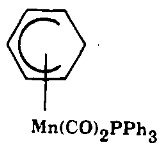
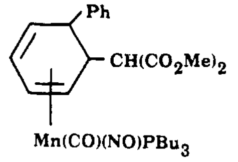


4



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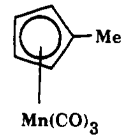

6

Note Added in Proof: We recently became aware of a study of the electrochemical oxidation of aromatic hydrocarbons in dichloromethane at temperatures down to −70 °C: Byrd, L.; Miller, L. L.; Pletcher, D. *Tetrahedron Lett.* **1972**, 2419. In this paper it was shown that the half-lives of aromatic hydrocarbon radical cations can be increased by 10^2–10^4 by lowering the temperature from ambient to −70 °C.

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[25] Anson, F. C. *Anal. Chem.* **1966**, *38*, 54. Christie, J. H.; Osteryoung, R. A.; Anson, F. C. *J. Electroanal. Chem.* **1967**, *13*, 236. Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*; Wiley: New York, 1980.

[26] Gosser, D. K.; Rieger, P. H., EZMULT, digital simulation program, to be submitted for publication.

Uranium–Carbon Multiple-Bond Chemistry. 8.[1] The Reaction of $W(CO)_6$ with $Cp_3U{=}CHP(Ph)(R)(Me)$ To Form $(OC)_5WC(OUCp_3)CHP(Ph)(R)(Me)$ and Its Isomerization to $Cp_3UOCH{=}CHP(Ph)(R)CH_2W(CO)_5$

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Summary: The reaction of $W(CO)_6$ with $Cp_3U{=}CHP(Ph)(R)(Me)$ yields the tungstaenolate $(OC)_5WC(OUCp_3)CHP(Ph)(R)(Me)$ (**3a**, R = Me; **3b**, R = Ph) which upon heating at 90 °C isomerizes to $Cp_3UOCH{=}CHP(Ph)(R)CH_2W(CO)_5$ (**4a**, R = Me; **4b**, R = Ph). This exchange of $W(CO)_5$ and hydrogen establishes a third type of carbonyl activation for $Cp_3U{=}CHP(Ph)(R)(Me)$. The crystal structures of **3b**$\cdot {}^1/_2C_7H_8$ (space group $P2_1/c$, unit-cell parameters a = 8.669 (1) Å, b = 10.576 (2) Å, c = 39.63 (2) Å, β = 98.38 (2)°, and V = 3595 (2) Å^3; R = 5.85%, R_G = 6.83%) and **4b** (space group $P2_1/c$, unit-cell parameters a = 17.176 (4) Å, b = 11.804 (2) Å, c = 17.588 (2) Å, β = 114.49 (1)°, and V = 3245 (1) Å^3; R = 4.19%, R_G = 4.59%) have been determined.

We have shown[2–4] that carbon monoxide which is co-

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[1] Part 7 of this series: Cramer, R. E.; Engelhardt, U.; Higa, K. T.; Gilje, J. W. *Organometallics* **1986**, *5*, 000–000.

[2] Cramer, R. E.; Higa, K. T.; Pruskin, S. L.; Gilje, J. W. *J. Am. Chem. Soc.* **1983**, *105*, 6749–6750.

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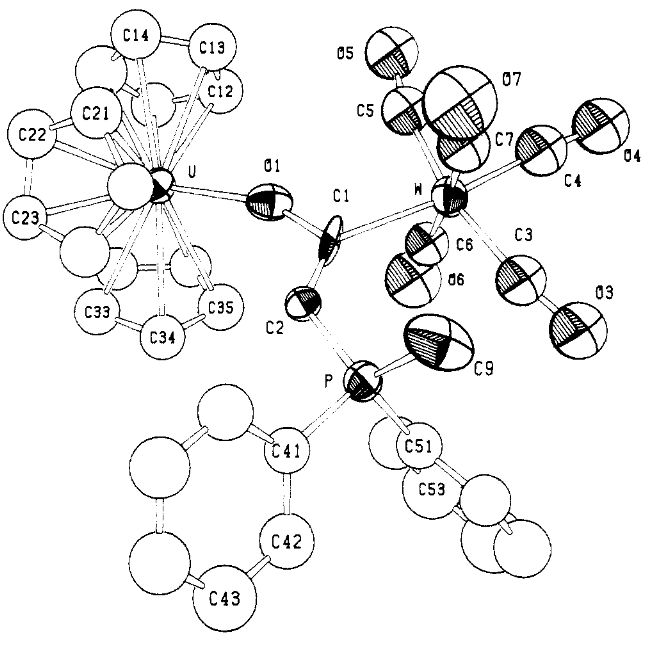


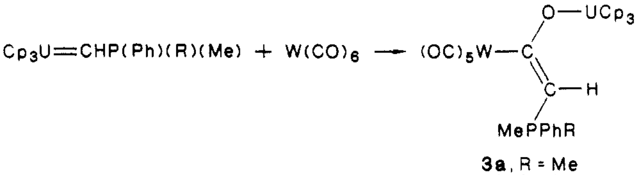
Figure 1. An ORTEP drawing of $(OC)_5WC(OUCp_3){=}CHPPh_2Me$ (**3b**). Some important bond distances (Å) and angles (deg): U–O1, 2.15 (2); O1–C1, 1.36 (3); C1–C2, 1.36 (3); C1–W, 2.26 (2); P–C2, 1.78 (2); P–C9, 1.81 (3); U–O1–C1, 158 (2); O1–C1–W, 116 (1), O1–C1–C2, 109 (2); C2–C1–W, 135 (2); P–C2–C1, 127 (2).

ordinated to a transition metal can be activated by insertion into the uranium–carbon multiple bond in $Cp_3U{=}CHP(Ph)(R)(Me)$ (**1a**. R = Me; **1b**. R = Ph), where Cp = η-$C_5H_5^-$, Me = CH_3, Ph = C_6H_5. Examples include the reaction of **1** with $CpMn(CO)_3$ where a carbonyl is deoxygenated and a new carbon–carbon triple bond is formed[4] and the reaction of **1** with $[CpFe(CO)_2]_2$ during which bridging and terminal carbonyls couple to produce an allyl group.[2] The first step in both of these reactions appears to be the insertion of a terminal carbonyl into the U=C bond of **1** to form a Cp_3U^+ coordinated phosphonium metallaenolate. The initial product in the $CpMn(CO)_3$ reaction is $Cp(OC)_2MnC(OUCp_3)CHP(Ph)(R)(Me)$ (**2a**, R = Me; **2b**, R = Ph),[3] and NMR peaks of the $MC(OUCp_3)CHP(Ph)(R)(Me)$ moiety can be observed[5] early in the reaction with $[CpFe(CO)_2]_2$. We now report that a similar insertion of $W(CO)_6$ into **1** forms a $-C(OUCp_3)CHP(Ph)(R)(Me)$ ligand which is structurally identical with the one in **2**. However, this product undergoes an unusual metal migration which we have not previously encountered for $MC(OUCp_3)CHP(Ph)(R)(Me)$ fragments, establishing a third type of carbonyl activation for **1**.

The reaction of $W(CO)_6$ with **1** in THF solution at room temperature for 4 days, followed by filtration yields a dark red compound, **3**,[6] in about 70% yield. This material can be isolated by benzene extraction of the residue remaining after evaporation of the THF solvent. X-ray quality single crystals of **3b** were grown from a THF solution onto which a 1:20 toluene–pentane mixture was layered.

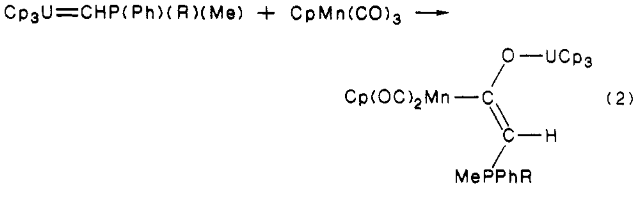
Crystals of $\mathbf{3b}\cdot{}^1/_2C_7H_8$ belong to the space group $P2_1/c$ with unit-cell parameters a = 8.669 (1) Å, b = 10.576 (2) Å, c = 39.63 (2) Å, β = 98.38 (2)°, and V = 3595 (2) Å^3. The structure of $\mathbf{3b}\cdot{}^1/_2C_7H_8$ was determined by X-ray diffraction,[7] and an ORTEP drawing of the molecule is shown in Figure 1. Crystallographic data are summarized in Table I (supplementary material). A complete listing of bond distances and angles appears in Table II, the positional and thermal parameters are listed in Table III, and the observed and calculated structure factors are in Table IV (supplementary material).

The reaction of **1** with $W(CO)_6$ (eq 1) is very similar to that of **1** with $CpMn(CO)_3$ (eq 2). The metrical parameters within the $-C(OUCp_3){=}CHP(Ph)(R)(Me)$ ligands in **2a**[3] and **3b** are identical within experimental uncertainty, and, consistent with our discussion[3] of the bonding in **2a**, a Cp_3U^+-coordinated phosphonium metallaenolate is written as the major resonance structure of **3**. The W–C(1) bond length of 2.26 (2) Å in **3b** can be compared with the W–C single-bond distance of 2.34 (1) Å in $[(OC)_5WCH(OMe)(Ph)]^-$ [8] and with the partial multiple-bond lengths of 2.14 (2) Å in $(OC)_5W{=}CPh_2$[9] and 2.18 (2) Å in $(OC)_5W{=}C(OC_2H_5)(C_5H_8CHCPh_2)$[10] and with the double bond of 1.98 (1) Å in $(DPPE)(OC)_3W{=}C{=}CHCO_2Me$.[11] W–C(1) in **3b** clearly lies between a single and double bond. The Mn–C bond in **2** also contains double-bond character.[3]



3a, R = Me
b, R = Ph

(1)



(2)

2

While **2** and **3** bear strong structural resemblance, they

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(3) Cramer, R. E.; Higa, K. T.; Gilje, J. W. *J. Am. Chem. Soc.* **1984**, *106*, 7245–7247, reports the reaction of **1a** with $CpMn(CO)_3$ and the structure of **2a**. A similar reaction occurs with **1b**.[5]

(4) Cramer, R. E.; Higa, K. T.; Gilje, J. W. *Organometallics* **1985**, *4*, 1140–1141, reports the structure of $Cp(OC)_2MnC{\equiv}CPMe_2Ph$ which results upon heating **2a**. A similar reaction occurs with **2b**.[5]

(5) Higa, K. T. Ph.D. Dissertation, University of Hawaii, 1985, and unpublished results.

(6) ^{1}H NMR (THF-d_8, 300 MHz): **3a**, δ 28.24 (d, 1 H, J_{PCH} = 25.7 Hz, PC*H*), 7.7 (mult, 3 H, Ph), 7.4 (mult, 2 H, Ph), 3.9 (d, 6 H, J_{PCH} = 13.4 Hz, *Me*P), -9.31 (s, 15 H, *Cp*$_3$U); **3b**, δ 26.01 (d, 1 H, J_{PCH} = 24.8 Hz, PC*H*), 8.81 (mult, 4 H, Ph), 8.5 (mult, 6 H, Ph), 2.66 (d, 3 H, J_{PCH} = 13.6 Hz, *Me*P), -8.91 (s, 15 H *Cp*$_3$U). IR (THF solution on NaCl plates, 1700–2100 cm^{-1}): 2049 (m), 1975 (s, sh), 1894 (vs), 1792 cm^{-1} (m, sh). Anal. Calcd: C, 44.27; H, 3.18. Found: C, 43.55; H, 3.35.

(7) Single crystals of **3b** and **4b** were mounted in glass capillaries and sealed under nitrogen. X-ray data were collected using a Syntex P$\bar{1}$ diffractometer. The heavy atoms were located using MULTAN-80, a system of computer programs for direct method solution of crystal structures from X-ray data by P. Main, 1980, and the remaining atoms were located in a series of difference Fourier maps and least-squares refinements using SHELX-76, a system of computer programs for X-ray structure determination by G. M. Sheldrick, 1976.

In **3b** the Cp groups, the phenyl rings, and the toluene solvate molecule were refined isotropically as rigid bodies using the standard parameters contained in SHELX-76. With the exception of the carbonyl groups which were also refined isotropically the remaining atoms were anisotropically refined. The final error indices were R = 5.85% and R_G = 6.83%.

For **4b** the Cp and phenyl groups were refined isotropically as rigid bodies; all remaining atoms were refined anisotropically to yield the final error indices of R = 4.19% and R_G = 4.59%.

(8) Casey, C. P.; Polichnowski, S. W.; Tuinstra, H. E.; Albin, L. D.; Calabrese, J. C. *Inorg. Chem.* **1978**, *17*, 3045–3049.

(9) Casey, C. P.; Burkhart, T. J.; Bunnett, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127–2134.

(10) Daran, J. C.; Jeannin, Y. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 1392–1395.

(11) Birdwhistell, K. R.; Nieter Burgmayer, S. J.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 7789–7790.

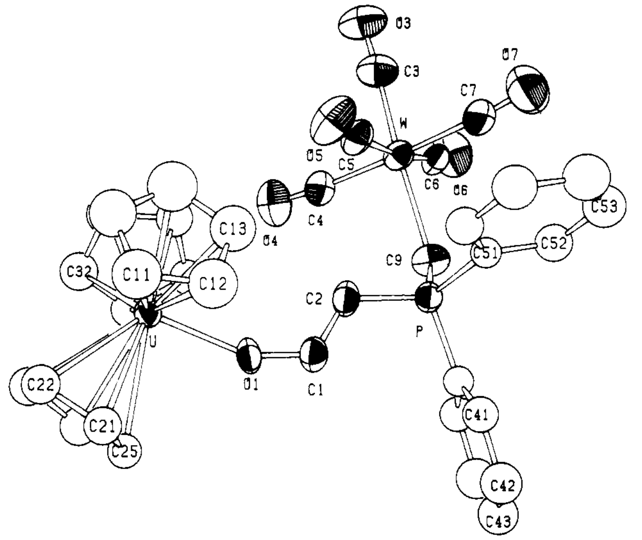
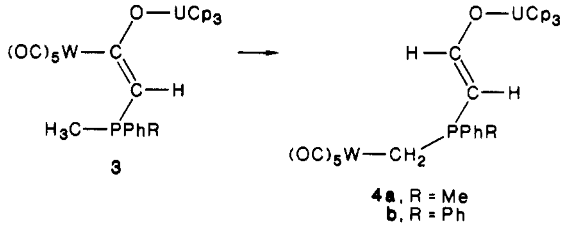


Figure 2. An ORTEP drawing of $Cp_3UOCH{=}CHPPh_2CH_2W(CO)_5$ (**4b**). Some important bond distances (Å) and angles (deg): U–O1, 2.207 (9); O1–C1, 1.31 (1); C1–C2, 1.37 (2); P–C2, 1.76 (1); P–C9, 1.79 (1); W–C9, 2.36 (1); U–O1–C1, 156.1 (8); O1–C1–C2, 123 (1); P–C2–C1, 124 (1); C2–P–C9, 110.1 (6); W–C9–P, 116.8 (7).

display different chemistries. When **2** is heated to 80 °C, the elements of Cp_3UOH are eliminated and $Cp(OC)_2MnC{\equiv}CP(Ph)(R)(Me)$ is formed in nearly quantitative yield.[4] While NMR peaks consistant with a $WC{\equiv}CPMePhR$ moiety[4,5,12] appeared when THF solutions of **3** were heated to 90 °C for 48 h, another compound, **4**,[13] was also produced. NMR and IR spectra of **4** indicate $W(CO)_5$, CpU, PPh, and HCP units.[13] However, **4** could not be unambiguously identified from these data so an X-ray crystal structure of **4b** was determined[7] using crystals (space group $P2_1/c$, unit-cell parameters a = 17.176 (4) Å, b = 11.804 (2) Å, c = 17.588 (2) Å, β = 114.49 (1)°, and V = 3245 (1) Å^3) precipitated from a THF solution onto which a 1:20 toluene–pentane mixture had been layered. An ORTEP of molecule **4b** is shown in Figure 2; a summary of the crystal, data collection, and refinement appears in Table I, a complete listing of bond distances and angles in Tables V, the positional and thermal parameters in Table VI, and the observed and calculated structure factors in Table VII (supplementary material).

The W–C(9) bond distance of 2.36 (1) Å indicates a single bond,[8] and the 1.37 (2) Å C(1)–C(2) separation is typical for a double bond. Other metrical parameters are normal for the resonance form drawn below for **4**. In both **3b** and **4b** the metrical parameters within the enolate portion of the ligands are indistiguishable from those in $Cp_2Ti(OCH{=}CH_2)_2$.[14]

Reaction 3 involves the interchange of hydrogen and $(OC)_5W$ moieties. While the mechanism of this reaction



(3)

has not been determined, NMR peaks of **3** disappear within 24 h at 90 °C leaving broad resonances which undergo complex changes, finally sharpening to the characteristic peaks of **4** after about 48 h. When solutions of **3** are heated in the presence of PPh_3, the rate of reaction is not markedly influenced and the final product is a phosphine complex which also can be obtained by heating solutions of **4** with PPh_3. These observations imply that the conversion occurs through several intermediates and probably does not involve $(OC)_5W$ dissociation. The mechanism of the reaction is still under study.

Overall the reaction of **1** with $W(CO)_6$ represents the conversion of a coordinated carbon monoxide to the enolate of an aldehyde and involves cleavage of the original W–C bond.

Acknowledgment. The support of this work by the National Science Foundation, Grants CHE82-10244 and CHE-8519289 (J.W.G. and R.E.C.) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. **1a**, 77357-85-8; **1b**, 77357-86-9; **3a**, 104807-99-0; **3b**, 104780-30-5; **4a**, 104808-00-6; **4b**, 104780-31-6; $W(CO)_6$, 14040-11-0.

Supplementary Material Available: Table I, crystal, data collection, and reduction parameters for $(OC)_5WC(OUCp_3)CHPPh_2Me{\cdot}{}^1/_2C_7H_8$ and $Cp_3UOCH{=}CHPPh_2CH_2W(CO)_5$, Table II, bond distances and bond angles for $(OC)_5WC(OUCp_3)CHPPh_2Me{\cdot}{}^1/_2C_7H_8$, Table III, positional and thermal parameters for $(OC)_5WC(OUCp_3)CHPPh_2Me{\cdot}{}^1/_2C_7H_8$, Table V, bond distances and bond angles for $Cp_3UOCH{=}CHPPh_2CH_2W(CO)_5$, and Table VI, positional and thermal parameters for $Cp_3UOCH{=}CHPPh_2CH_2W(CO)_5$ (5 pages); Table IV, observed and calculated structure factors for $(OC)_5WC(OUCp_3)CHPPh_2Me{\cdot}{}^1/_2C_7H_8$, and Table VII, observed and calculated structure factors for $Cp_3UOCH{=}CHPPh_2CH_2W(CO)_5$ (34 pages). Ordering information is given on any current masthead page.

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[12] (a) Kaska, W. C.; Mitchell, D. K.; Reichelderfer, R. F.; Korte, W. D. *J. Am. Chem. Soc.* **1974**, *96*, 2847–2854. (b) Kaska, W. C.; Mitchell, D. K.; Reichelderfer, R. F. *J. Organomet. Chem.* **1973**, *47*, 391–402. (c) Blau, H.; Griessman, K.-H.; Malish, W. *J. Organomet. Chem.* **1984**, *263*, C5–C9.

[13] NMR spectra taken on reactions run in THF-d_8 at 90 °C show about equal conversion to the $-C{\equiv}CPMePhR$-containing compound and to **4**. An isolated yield of 32% was obtained after recrystallization of **4b**. ^1H NMR (THF-d_8, 300 MHz): **4a**, δ 6.02 (mult, 1 H, Ph), 5.33 (mult, 2 H, Ph), 1.57 (mult, 2 H, Ph) –4.04 (s, 15 H, *Cp*$_3$U), –4.83 (d, 3 H, J_{PCH} = 12.8 Hz, *MeP*), –5.21 (dd, 1H, J_{PCH} = 14 Hz, J_{HCH} = 14 Hz, H_aH_bCP, H_a), –5.91 (dd, 1 H, J_{PCH} = 14 Hz, J_{HCH} = 14 Hz, H_aH_bCP, H_b), –11.51 (dd, 1 H, J_{PCH} = 13.6 Hz, J_{HCCH} = 12.6 Hz, PC*H*=), –26.55 (dd, 1 H, J_{PCCH} = 8.4 Hz, J_{HCCH} = 12.6 Hz, OC*H*=); **4b**, 5.87 (mult, 2 H, Ph), 5.13 (mult, 4 H, Ph), 1.18 (mult, 4 H, Ph) –3.83 (s, 15 H, *Cp*$_3$U), –5.00 (d, 2 H, J_{PCH} = 15.2 Hz, H_2C), –11.24 (dd, 1 H, J_{PCH} = 14.8 Hz, J_{HCCH} = 10.6 Hz, PC*H*=), –27.24 (dd, 1 H, J_{PCCH} = 7.7 Hz, J_{HCCH} = 10.6 Hz, OC*H*=). IR (THF solution on NaCl plates, 1800–2100 cm^{-1}): 2051 (m), 1958 (s, sh), 1892 (vs), 1863 cm^{-1} (s). Anal. Calcd: C, 42.10; H, 2.93. Found: C, 42.93; H, 3.61.

[14] Curtis, M. D.; Thanedar, S.; Butler, W. M. *Organometallics* **1984**, *3*, 1855–1859.

Intra- and Intermolecular Activation of sp^2 C–H Bonds at Rhodium(I) and Iridium(I) Metal Centers. X-ray Structure of the Cis σ-Cyclooctadienyl Hydride $[\{N(CH_2CH_2PPh_2)_3\}IrH(\sigma\text{-}C_8H_{11})]BPh_4{\cdot}CH_3COCH_3$

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Maurizio Peruzzini, Michal Sabat, and Fabrizio Zanobini

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Summary: The metal–ligand fragment $[(np_3)Ir]^+$ [np_3 = $N(CH_2CH_2PPh_2)_3$] intermolecularly activates one sp^2 C–H

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