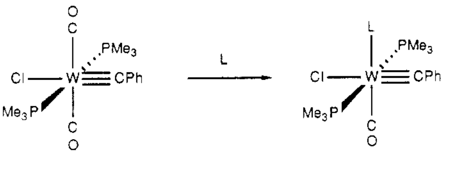
are a high-energy infrared stretch at 2015 cm^{-1} and a ^{13}C NMR resonance at δ 172 for the ketenyl carbonyl group. The signal for the terminal ketenyl carbon atom (Ph*C*CO) was not found. The only previously reported ketenyl alkyne metal complex [W(η^5-C_5H_5)(η^1-*p*-MeC_6H_4CCO)(CO)($Et_2NC{\equiv}CMe$)] was obtained by Kreissl in the the thermal reaction of [W(η^2-*p*-MeC_6H_4CCO)(Cl(CO)(PMe_3)] with the alkyne.[18] Complex 11 does not form thermally even by reaction of 2 with neat phenylacetylene.

The trans isomers of the bis(phosphine)-substituted metal carbyne complexes are easily susceptible to substitution of one carbonyl ligand. This increased reactivity compared to the cis isomers is a consequence of the mutual trans orientation of the two π-acceptor carbon monoxide ligands. For example, reaction of complex 5 with trimethylphosphine for 1 h in methylene chloride solution at 40 °C and reaction in neat pyridine for 24 h at room temperature gives the known compounds [W(≡CPh)Cl(CO)(PMe_3)$_3$][16] and [W(≡CPh)Cl(CO)(py)(PMe_3)$_2$][16] in 70 and 90% spectroscopic yields, respectively. Reaction of 5 in CH_2Cl_2 with a few drops of concentrated aqueous HCl gives [W(=CHPh)Cl_2(CO)(PMe_3)$_2$][16] spectroscopically pure after treatment of the organic phase with Na_2CO_3 and $MgSO_4$.



(2)

5

L = PMe_3, pyridine

Acknowledgment. This work was supported by the National Science Foundation (CHE 8617472) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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[17] 11: ^1H NMR ($CDCl_3$, 223 K) δ 13.0 (s, 1 H, PhCC*H*), 8.4 (d, 2 H, C_6H_5), 7.5–7.1 (m, C_6H_5), 1.2 (t, 18 H, PMe_3); ^{13}C NMR ($CDCl_3$, 223 K) δ 228.9 (J_{CW} = 132.8 Hz, CO), 208.6 (Ph*C*CH), 203.7 (J_{CH} = 206.6 Hz, PhC*C*H), 172.4 (PhC*C*O), 16.1 (J_{CP} = 14.3 Hz, P(CH_3)$_3$); ^{31}P NMR ($CDCl_3$, 223 K) δ -23.0 (PMe_3); IR (CH_2Cl_2) ν_{PhCCO} 2015 (s), ν_{CO} 1940 (s) cm^{-1}.

[18] Kreissl, F. R.; Reber, G.; Müller, G. *Angew. Chem.* 1986, *98*, 640–641.

(Pentadienyl)molybdenum Carbonyl Chemistry: Conversion of a Pentadienyl Ligand to a Coordinated Metallabenzene Complex

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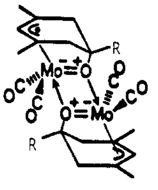
Received July 1, 1987

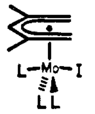
Summary: Reaction of 2 equiv of the (2,4-dimethylpentadienyl)molybdenum tricarbonyl anion with IC_2H_4I leads to the formation of $Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_5$ which has been characterized spectroscopically and through an X-ray diffraction study. Bonding parameters indicate that a Mo(2,4-C_7H_9) unit functions as a molybdabenzene fragment η^6 coordinated to the other molybdenum atom.

Recently we reported an entry into (pentadienyl)molybdenum carbonyl chemistry via the Mo(2,4-C_7H_{11})(CO)$_3$ anion (C_7H_{11} = dimethylpentadienyl).[2] Quite surprisingly, this anion was found to react with methyl iodide to yield an unusual coupling product, 1 (R = CH_3), rather than the expected metal alkyl complex Mo(2,4-C_7H_{11})(CH_3)(CO)$_3$, cf., Mo(C_5H_5)(CH_3)(CO)$_3$.[3] As there would seem to be a possibility that this type of reaction might have some useful applications, we have examined related reactions designed to probe the generality of this coupling process. In addition to some straightforward transformations, we now report an unusual reaction with diiodoethane, which leads to a product which appears best formulated as an (η^6-metallabenzene)metal complex.



1

The Mo(2,4-C_7H_{11})(CO)$_3$ anion, readily prepared from Mo(diglyme)(CO)$_3$ and K(2,4-C_7H_{11}), may be easily isolated as crystalline K(diglyme)$^+$Mo(2,4-C_7H_{11})(CO)$_3^-$ following toluene extraction.[4] This species undergoes clean reactions with Hg(CN)$_2$, AgI, and I_2, leading to Hg[Mo(2,4-C_7H_{11})(CO)$_3$]$_2$, [Mo(2,4-C_7H_{11})(CO)$_3$]$_2$, and Mo(2,4-C_7H_{11})(I)(CO)$_3$ in good yields.[5] All of these complexes have been characterized analytically and spectroscopically, and an X-ray diffraction study of the iodide complex has revealed its configuration to be that of 2.[6]



2

As in the case of methyl iodide, ethyl iodide reacts with Mo(2,4-C_7H_{11})(CO)$_3^-$ to yield a coupled product (1, R = Et). Reaction with 1,2-diiodoethane, however, yields a product which spectroscopically differs significantly from 1 and furthermore appeared to lack some expected resonances in its NMR spectra. Infrared spectroscopy revealed that all CO ligands were terminally bound, and isopiestic molecular weight determinations indicated a dimetallic structure,[7] but resort to diffraction methods was necessary for a structural assignment.[8]

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[1] (a) University of Utah. (b) University of Delaware.

[2] Kralik, M. S.; Hutchinson, J. P.; Ernst, R. D. *J. Am. Chem. Soc.* 1985, *107*, 8296.

[3] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* 1956, *3*, 104.

[4] (a) In addition to routine spectroscopic and analytical data, the compound has been characterized by a single-crystal X-ray diffraction study which reveals a polymeric, isocarbonyl complex. (b) Kralik, M. S.; Rheingold, A. L.; Ernst, R. D., unpublished results.

[5] In each case, reactions were carried out in THF at low temperatures and the products subsequently extracted with hexane after THF removal in vacuo. Yields were 90%, 45%, and 60%, respectively. Experimental details and spectroscopic data for all compounds are included in the supplementary material.

[6] (a) Unfortunately, the structure was subject to an apparent disorder, possibly the result of a twinned crystal. (b) Rheingold, A. L., unpublished results.

[7] Calculated molecular weight (isopiestic, THF): 520. Found: 530. Anal. Calcd for $C_{19}H_{20}Mo_2O_5$: C, 43.87; H, 3.87. Found: C, 44.38; H, 4.12. IR (pentane solution, CO region): 2037 (s), 1996 (s), 1942 (m), 1928 (s), 1907 (s) cm^{-1}. Melting point: 142–144 °C.

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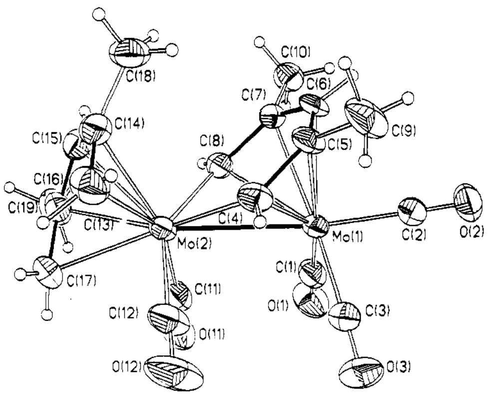
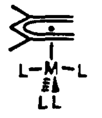


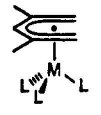
Figure 1. Perspective view and numbering scheme for $Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_5$. Distances from Mo(1) to the C(4)–C(8) atoms are 2.297 (5), 2.377 (5), 2.329 (4), 2.369 (4), and 2.310 (4) Å, respectively, while the C–C distances in the C(4)–C(8) fragment are 1.418 (7), 1.424 (6), 1.410 (7), and 1.404 (6) Å, respectively.

The structural result, in which all hydrogen atoms could be located and refined, demonstrated that the complex had the formulation $Mo_2(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_9)(CO)_5$, in which one of the 2,4-dimethylpentadienyl ligands has lost a hydrogen atom from each of its terminal carbon atoms (Figure 1). In this complex, the coordination environments of the two metal centers differ significantly. Mo(2) is η^5-bound by one pentadienyl ligand (C(13)–C(17)), with Mo(2)–C distances ranging from 2.319 (5) to 2.355 (6) Å. Two carbonyl ligands are also attached, bringing the electron count on Mo(2) to 15. The 18-electron count on Mo(2) is reached by the formation of single bonds to C(4), C(8), and Mo(1) (2.150 (5), 2.161 (4), and 2.989 (1) Å, respectively). Ignoring the Mo(1)–Mo(2) bond, the coordination environment around Mo(2) is similar to that in I, the expected geometry of a M(pentadienyl)L_4 moiety.[9]

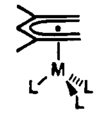


I

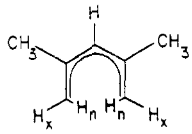
Somewhat more interesting is the coordination environment around Mo(1). One way to describe this would involve Mo(1) σ bound to Mo(2), η^5-bound by the pentadienyl fragment C(4)–C(8) (with bond distances ranging from 2.297 (5) to 2.377 (5) Å), and bound by its three terminal carbonyl ligands. Notably, two of the carbonyl ligands on Mo(1) are nearly eclipsed with the two carbonyl ligands on Mo(2), suggesting that in the Mo(1) coordination sphere at least, the Mo–Mo bond is exerting some stereochemical activity, as M(pentadienyl)L_3 complexes invariably adopt configuration II, with that of III being much higher in energy.[10] Hence, one could also describe the Mo(1) coordination sphere as being similar to I. However, several geometric features related to the C(4)–C(8) fragment suggest a different formulation.



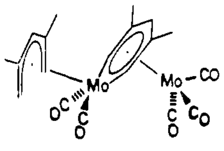
II



III



First, it can be noted that in η^5-bound pentadienyl ligands the endo (internal) substituents on the terminal carbon atoms tend to tilt significantly (ca. 45–50°) out of the pentadienyl ligand plane away from the metal atom,[11] as can be seen for C(13) and C(17). Similarly, the exo substituents tend to bend down toward the metal atom, generally by ca. 15–20°. However, Mo(2) lies essentially in the C(4)–C(8) plane, as do the exo hydrogen atoms located on C(4) and C(8). Secondly, one can observe some evidence for partial multiple bonding from Mo(2) to C(4) and C(8). Thus, while the bonds from Mo(2) to the pentadienyl carbon atoms (2.335 (3) Å) and to the carbonyl carbon atoms (2.030 (4) Å) are quite similar to the Mo–C(C_5H_5) (2.38 (2) Å) and Mo–CO (1.97 Å) distances in $Mo(C_5H_5)(C_2H_5)(CO)_3$,[12] the Mo(2)–C(4) and Mo(2)–C(8) distances are significantly shorter on the average (2.156(3) Å)[13] compared to the Mo–C_2H_5 distance of 2.38 Å in $Mo(C_5H_5)(C_2H_5)(CO)_3$. Structurally, at least, this complex seems better formulated as an (η^6-metallabenzene)metal complex, IV.[14] Mo(1) may therefore be regarded as being coordinated by the molybdenabenzene fragment generated by Mo(2) and C(4)–C(8).



IV

The spectral features, particularly the variable-temperature NMR behavior, may now be understood in the light of the structural result. At room temperature and a field strength of 300 MHz, there is clear evidence of proton site exchange in that two very broad resonances are observed. By 80°, these have mostly become reasonably sharp, and a 2:1:1:2:6:6:2 pattern is observed, consistent with the presence of symmetrical 2,4-C_7H_{11} and 2,4-C_7H_9 ligands.[15] Notably, while the hydrogen atoms on the central (3-position) carbon atoms are virtually always the

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(8) For $C_{19}H_{20}O_5Mo_2$: monoclinic, $P2_1/n$, a = 8.039 (2) Å, b = 17.873 (5) Å, c = 14.019 (3) Å, β = 98.02 (2)°, V = 1995 (1) Å^3, Z = 4, D(calcd) = 1.732 g cm^{-3}, μ(Mo Kα) = 12.5 cm^{-1}. Of 3799 reflections collected (4° ≤ 2θ ≤ 50°, ±h,+k,+l, Nicolet R3 diffractometer, 293 K), 3513 were independent and systematically present (R_{int} = 3.7%), and 2827 with $F_o \geq 3\sigma(F_o)$ were considered observed. The data were empirically corrected for absorption (T_{max}/T_{min} = 0.51/0.47). The structure was solved from a Patterson synthesis. All non-hydrogen atoms were anisotropically refined, and all hydrogen atoms were found and isotropically refined. At convergence: $R(F)$ = 3.64% [all data, 4.70%], $R(wF)$ = 4.59%, GOF = 1.134, Δ/σ = 0.068, $\Delta(\rho)$ = 0.81 [0.92 Å from Mo(2)], and N_o/N_v = 9.0. SHELXTL (5.1) (Nicolet Corp., Madison, WI) was used for all computations.

(9) Albright, T. A.; Hoffmann, R.; Tse, Y.-C.; D'Ottavio, T. *J. Am. Chem. Soc.* **1979**, *101*, 3812.

(10) (a) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (b) Albright, T. A. *Acc. Chem. Res.* **1982**, *15*, 149.

(11) Ernst, R. D. *Struct. Bonding* (Berlin) **1984**, *57*, 1.

(12) Bennett, M. J.; Mason, R. *Proc. Chem. Soc.* **1963**, 273.

(13) When average values are cited, the accompanying standard deviation is that of the mean, obtained by dividing the average deviation by the square root of the number of data. Such estimated standard deviations will reflect the uncertainty in the average value but will not necessarily reflect the distribution of the individual values.

(14) (a) An interesting theoretical treatment of metallabenzene, metallacyclopentadiene, and (η^5-metallacyclopentadienyl)metal complexes has been presented.[14b] (b) Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39.

(15) NMR (^{1}H, toluene-d_8, 80 °C): δ 7.66 (br s, 2 H), 5.90 (t, 1 H, J = 1.4 Hz), 4.90 (s, 1 H), 2.55 (d of d, 2 H, J = 1.6, 3.2 Hz), 1.89 (s, 6 H), 1.41 (s, 6 H), 0.66 (d, 2 H, J = 3.2 Hz).

furthest downfield resonance(s) for η^5-2,4-dimethylpentadienyl ligands,[16] one can observe that one resonance is even further downfield—this may readily be assigned to the two terminal hydrogen atoms on the C_7H_9 ligand. By -50 °C, one observes a 1:1:1:1:1:1:3:3:3:3:1:1 pattern,[17] consistent with the placement of both organic ligands in unsymmetric environments, such as in the observed structure. On the basis of this structure, one would expect that rotation of the C_7H_{11} ligand alone should restore the spectral symmetry. In accord with this, the values of ΔG^* for all five pairs of resonances are essentially identical at 12.6 ± 0.15 kcal/mol.[18] This value is quite similar to those observed in a variety of both mono(pentadienyl)- and bis(pentadienyl)metal complexes.[16,19]

In general, the loss of hydrogen substituents from terminal pentadienyl ligand sites should be expected to provide for some interesting conversions, as metallacyclohexadiene,[20] metallabenzene,[21] and cyclopentadienyl[22] complexes could easily result.[23] In fact, mass spectra of some "half-open metallocenes" show prominent peaks corresponding to loss of H_2, while some "open metallocenes" show prominent peaks corresponding to loss of $2H_2$.[24] It can easily be envisioned that these H_2 losses are accompanied by the conversion of pentadienyl to cyclopentadienyl ligands. In another example, the attempted preparation of a (pentadienyl)iridium compound led instead to a (hydrido)iridacyclohexadiene complex, $HIr(C_7H_{10})(PEt_3)_3$, which could be converted to a cyclopentadienyl complex following hydride abstraction.[20b] However, metallabenzene complexes have to date not been isolated from pentadienyl complexes and are rather rare species that may themselves be readily converted to cyclopentadienyl complexes.[21,22] In the present case, the survival of the metallabenzene unit may be dependent on the fact it is η^6-bound to the Mo(1) atom, and while one might expect a reductive elimination to lead to a cyclopentadienyl complex, we have not yet observed such a transformation to take place. For example, addition of phosphine or phosphite ligands seems to bring about CO substitution instead.[25] Further studies designed to probe the reaction chemistry of this unusual system are in progress.

Acknowledgment. R.D.E. is grateful to the National Science Foundation for generous support of this research.

Supplementary Material Available: Synthetic, spectroscopic, and analytical details for all new compounds, as well as a complete description of the crystallographic study, including tables of atomic parameters and pertinent bond distances and angles (17 pages); the structure factor tables (21 pages). Ordering information is given on any current masthead page.

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[16] (a) Wilson, D. R.; DiLullo, A. A.; Ernst, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5928. (b) Liu, J.-Z.; Ernst, R. D. *Ibid.* **1982**, *104*, 3737. (c) Wilson, D. R.; Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1983**, *2*, 1220.

[17] NMR (^1H, toluene-d_8, −80 °C): δ 8.31 (s, 1 H), 6.91 (s, 1 H), 5.74 (s, 1 H), 4.11 (s, 1 H), 2.31 (s, 1 H), 2.20 (s, 1 H), 1.84 (s, 3 H), 1.79 (s, 3 H), 1.47 (s, 3 H), 0.61 (s, 3 H), 0.28 (s, 1 H), 0.16 (s, 1 H). The underlined resonances are those which do not undergo exchange processes since they are located on the central carbon atoms. Note that one of these shows a strong temperature dependence. NMR (^{13}C, toluene-d_8, −80 °C): δ 228.1 (s, 1 C), 226.2 (br s, 3 C), 220.2 (s, 1 C), 165.9 (d, 1 C, J = 141 Hz), 154.5 (d, 1 C, J = 142 Hz), 117.5 (s, 1 C), 111.4 (s, 1 C), 110.8 (s, 1 C), 108.0 (s, 1 C), 103.3 (d, 1 C, J = 160 Hz), 97.0 (d, 1 C, J = 161 Hz), 65.9 (t, 1 C, J = 156 Hz), 55.9 (t, 1 C, J = 159 Hz), 28.9 (q, 1 C, J = 126 Hz), 28.4 (q, 1 C, J = 127 Hz), 28.0 (q, 1 C, J = 127 Hz), 25.2 (q, 1 C, J = 126 Hz). The large downfield shifts for two of the CH resonances (at 165.9 and 154.5 ppm) indicate that these arise from the terminal carbon atoms of the C_7H_9 ligand.

[18] (a) It can be noted that every higher temperature resonance which decoalesces leads to two adjacent resonances at low temperatures; i.e., the frequency separations happen to be small enough that no other resonance falls between them. For the five pairs of low-temperature resonances, the frequency separations (Hz) and coalescence temperatures, from low to high field, are (420.2, 9 °C), (33.3, −20°), (14.5, −28 °C), (259.0, 0 °C), and (34.4, −18 °C), corresponding to ΔG^* values (±0.3 kcal/mol) of 12.6, 12.6, 12.6, 12.5, and 12.7 kcal/mol, respectively. (b) ΔG^* (J/mol) = $19.13(T_c)(9.97 + \log T_c/\delta\nu)$.[17c] (c) Günther, H. *NMR Spectroscopy*; Wiley: New York, 1980; p 243.

[19] (a) Stahl, L.; Ernst, R. D. *Organometallics* **1983**, *2*, 1229. (b) Bleeke, J. R.; Stanley, G. G.; Kotyk, J. J. *Ibid.* **1986**, *5*, 1642. (c) Whitesides, T. H.; Budnik, R. A. *Inorg. Chem.* **1975**, *14*, 664.

[20] (a) Grabowski, N. A.; Hughes, R. P.; Jaynes, B. S.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1694. (b) Bleeke, J. R.; Peng, W.-J. *Organometallics* **1987**, *6*, 1576. (c) Egan, J. W., Jr.; Hughes, R. P.; Rheingold, A. L. *Ibid.* **1987**, *6*, 1578.

[21] Elliot, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811.

[22] (a) Ferede, R.; Allison, N. T. *Organometallics* **1983**, *2*, 463. (b) See also: Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808.

[23] As the observed product formally results from the loss of C_2H_4, H_2, CO, and 2KI from the starting materials, one might readily speculate on the other products formed during the reaction. Spectral examination of the gaseous hydrocarbon product revealed the presence of ethylene and the absence of ethane. At this stage a mechanism for the metallabenzene complex formation can only be speculated. Actually, a number of possible pathways could be followed. If a complex having two $Mo(C_7H_{11})(CO)_3$ units bridged by C_2H_4 is initially formed, an η^5–η^3 pentadienyl conversion could be followed by an oxidative addition of a terminal C–H bond to the 16-electron molybdenum center. β-elimination of either molybdenum unit to the other, accompanied by either an η^5–η^3 or η^3–η^1 ligand conversion, could lead to an ethylene complex, after which the ethylene could be lost. Subsequent steps involving oxidative additions of Mo–C and C–H bonds to molybdenum centers could ultimately lead to the observed product (with elimination of H_2 and CO). One of the many other alternatives involves CO loss occurring as a first step, followed by steps similar to those described above. Future labeling studies should partially help to understand the process by which the complex was formed.

[24] (a) The abundance of such ions is very dependent on the ionizing potential, but nonetheless such peaks are quite significant in species such as $V[1,5-(SiMe_3)_2C_5H_5]_2$, $V(C_5H_5)[1,5-(SiMe_3)_2C_5H_5]$, $Cr(2,4-C_7H_{11})_2$, and $Cr(C_5Me_5)(C_5H_7)$, as well as a wide variety of other related complexes.[24b] (b) Freeman, J. W.; Gedridge, R. W.; Ernst, R. D., unpublished results.

[25] Kralik, M. S.; Ernst, R. D., unpublished results.

Synthesis and First Structural Characterization of Transition-Metal Complexes Containing η^1-*cis*-Pentadienyl and η^1-*trans*-Pentadienyl Ligands[1]

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Received July 30, 1987

Summary: Reaction of $(\eta^5$-pentadienyl$)Re(CO)_3$ with PEt_3 in refluxing diethyl ether produces (*fac*-η^1-*cis*-pentadienyl)$Re(CO)_3(PEt_3)_2$ (**1a**), which slowly converts to its η^1-*trans*-pentadienyl isomer, **1b**. Analogous products, **2a** and **2b**, are produced under similar conditions in the PMe_3 system. When **2** is reacted with additional PMe_3 in refluxing *tetrahydrofuran*, carbonyl substitution occurs and (*mer*-η^1-*trans*-pentadienyl)$Re(CO)_2(PMe_3)_3$ (**3**) is produced. Both **1a** and **3** have been structurally characterized.

During the past several years, there has been increasing interest in the synthesis and reactivity of pentadienyl–transition-metal complexes.[2] One reason for this interest

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[1] Pentadienyl-Metal-Phosphine Chemistry. 14. For the previous two papers in this series, see: (a) Bleeke, J. R.; Donaldson, A. J.; Peng, W.-J. *Organometallics* 1987, *6*, xxxx. (b) Bleeke, J. R.; Peng, W.-J. *Ibid.* 1987, *6*, 1576.

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