C, 63.58; H, 4.39; N, 1.57. Found: C, 63.43; H, 4.36; N, 1.46.

Reaction of HBF$_4$/Et$_2$O with 2a or 2b. A. Without Added Phosphine: Synthesis of Fe$_2$(CO)$_6$(μ-CHCPhCPhH) (6). To 1 g of **2a** or **2b** in dichloromethane solution at 0 °C was added a slight excess of HBF$_4$/Et$_2$O. The solution turned dark red and was evaporated to dryness. Extraction of the residue with pentane (3 × 10 mL), concentration, and cooling to −20 °C gave **6** as dark red crystals in 30% yield; IR ν(CO) (hexane solution) 2060 s, 2020 vs, 1994 vs, 1985 vs, 1970 m, 1962 m cm^{-1}; ^{1}H NMR (CDCl$_3$ solution) 8.36 (d (J = 2.4 Hz, 1 H), 7.28 m (9 H), 4.87 d (J = 2.4 Hz) + m (2 H). Anal. Calcd for C$_{21}$H$_{12}$O$_6$Fe$_2$: C, 53.38; H, 2.54. Found: C, 53.53; H, 2.67. Mass spectrum, m/z = 472.

B. With Added Phosphine. To a solution of 1 g of **2b** and 0.3 g of PPh$_3$ (or 17 μL of PMe$_2$Ph) in dichlormethane at 0 °C was added a slight excess of HBF$_4$/Et$_2$O. The solution was evaporated to dryness. Extraction of the residue with pentane and crystallization at −20 °C gave the following:

(i) With PPh$_3$, **7** as orange crystals in 50% yield; IR ν(CO) (hexane solution) 2059 m, 2018 s, 1994 m cm^{-1}; ^{1}H NMR (CDCl$_3$ solution) 7.33 m (25 H), 6.06 d (J = 9.4, 1 H), 3.90 d (J = 9.4, 1 H); ^{13}C NMR (CDCl$_3$ solution) (except phenyl resonances) 215.2 d (J_{PC} = 19 Hz, CO), 212.7 s (CO), 156.9 s (CPh), 98.2 d (J = 157 Hz, CH), 68 d (J = 157.4, CHPh). Anal. Calcd for C$_{39}$H$_{27}$O$_6$PFe$_2$: C, 63.76; H, 3.68. Found: C, 63.52; H, 3.76. Mass spectrum, m/z = 626.

(ii) With PMe$_2$Ph, **8**, as orange crystals (30% yield); IR ν(CO) (hexane solution) 2040 m, 2000 s, 1963 m cm^{-1}; ^{1}H NMR (CDCl$_3$ solution) 7.34 (15 H), 5.90 dd (J_1 = 9.3 Hz, J_2 = 2.4 Hz), 3.77 d (J = 9.3 Hz, 1 H), 1.87 d (J = 9.1 Hz, 3 H), 1.86 d (J = 9.1 Hz, 3 H). Anal. Calcd for C$_{29}$H$_{23}$O$_6$PFe$_2$: C, 57.04; H, 3.77. Found: C, 56.64; H, 3.89. Mass spectrum, m/z = 610.

X-ray Structure Analysis of [PPh$_4$][Fe$_2$(CO)$_6$(μ-C(OEt)-H)(μ-CPhCPhH)] (2b). Crystals belong to the triclinic system, space group $\bar{P}1$. The crystal was sealed on a glass fiber and mounted on a Philips PW-1100 diffractometer. Unit-cell parameters were determined from 25 reflections ($4 \leq \theta \leq 12°$) and refined by least-squares technique. A summary of crystal and intensity collection data is given in Table II. Three reflections were measured every 2 h as orientation and intensity control. Significant intensity decay was not observed. A total of 2786 reflections were measured in the range $2 \leq \theta \leq 25°$, 2663 of which were assumed as observed applying the condition $I \geq 2.5\sigma(I)$. Lorentz–polarization corrections were made, but not absorption corrections.

The Fe atoms were located from a Patterson synthesis, and the remaining non-hydrogen atoms from a subsequent weighted Fourier synthesis. The structure was refined by least-squares method using the SHELX-76 computer program.[17] The function minimized was $\sum w||F_o| - |F_c||^2$, where $w = (\sigma^2|F_o| + 0.0054|F_o|^2)^{-1}$. The final R value was 0.053 (Rw = 0.056) for all observed reflections. The fractional atomic coordinates of the non-hydrogen atoms are listed in Table III.

Supplementary Material Available: A table of anisotropic thermal parameters for [PPh$_4$][Fe$_2$(CO)$_6$(μ-CH(OEt))(μ-CPhCPhH)] (2b) (1 page); a table of structure factors for 2b (12 pages). Ordering information is given on any current masthead page.

(17) Sheldrick, G. M. SHELX-76 *Program for Crystal Structure Determination*; University of Cambridge, 1976.

Reaction of (η^5-C$_{13}$H$_9$)Mn(CO)$_3$ with Alkylphosphines: Formation and Isolation of η^1-Fluorenyl Complexes

Richard N. Biagioni,[*,1] Ivan M. Lorkovic, Jeffrey Skelton, and Jack B. Hartung

Department of Chemistry, Grinnell College, Grinnell, Iowa 50112

Received January 9, 1989

Reaction of (η^5-C$_{13}$H$_9$)Mn(CO)$_3$ with L = PEt$_3$ or PBu$_3$ leads to formation of (η^1-C$_{13}$H$_9$)Mn(CO)$_3$L$_2$. The L = PEt$_3$ complex was isolated analytically pure in moderate yield and characterized as the trans-meridional isomer by ^{1}H, ^{31}P, and ^{13}C NMR and IR spectroscopies. (η^1-C$_{13}$H$_9$)Mn(CO)$_3$L$_2$ decomposes via Mn–C bond homolysis to the C$_{13}$H$_9$ radical and Mn(CO)$_3$L$_2^{\bullet}$, which reacts further to yield HMn(CO)$_3$L$_2$. (η^1-C$_{13}$H$_9$)Mn(CO)$_3$L$_2$ can also be prepared by reacting L with (η^6-C$_{13}$H$_9$)Mn(CO)$_3$, apparently via a novel η^6 to η^1 shift.

Introduction

The ability of η^5-Cp and related ligands to undergo haptotropic shifts to η^3 or η^1 coordination, facilitating substitution reactions, is well established and has recently been reviewed by O'Connor and Casey.[2] In particular, the greater reactivity of indenyl and fluorenyl complexes compared to that of Cp complexes has stimulated interest in their application to synthesis and catalysis.[3] At the start of this work, the number of well-characterized η^1-cyclopentadienyl and η^1-indenyl complexes formed by ring slippage of η^5 complexes was quite limited, and there were

no well-documented examples of η^1-fluorenyl complexes. Our interest in the reactivity of such complexes led us to attempt to isolate new examples of η^1-indenyl and fluorenyl complexes.

In 1984, Ji, Rerek, and Basolo[4] reported on the reaction of (η^5-C$_{13}$H$_9$)Mn(CO)$_3$ (I) with L = PBu$_3$ (Bu = n-butyl throughout this report). At low PBu$_3$ concentrations, the reaction proceeded cleanly to the monosubstituted complex (η^5-C$_{13}$H$_9$)Mn(CO)$_2$L (IIa, L = PBu$_3$), by second-order kinetics, presumably via an unobserved η^3-fluorenyl intermediate, (η^3-C$_{13}$H$_9$)Mn(CO)$_3$PBu$_3$. However, at higher concentrations of PBu$_3$, a long-lived green intermediate and a different, yellow final product were observed. The

(1) Current address: Chemistry Department, Southwest Missouri State University, Springfield, MO 65804-0089.
(2) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307–318.
(3) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908–5912.

(4) Ji, L.-N.; Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740–745.

yellow final product, which could only be isolated as an impure oil, was characterized as $(\eta^5\text{-}C_{13}H_9)Mn(CO)(PBu_3)_2$, based primarily on IR (decalin, $\nu_{CO} = 1898$ cm^{-1}) and ^{31}P NMR spectroscopies ($\delta = 42.9$ ppm). A separate experiment starting with isolated IIa indicated that the reaction of IIa with PBu$_3$ was too slow to account for the observed rate of formation of the final product, ruling out a process involving two sequential substitutions. Therefore, an additional reaction pathway was proposed in which the transient $(\eta^3\text{-}C_{13}H_9)Mn(CO)_3PBu_3$ was trapped by a second PBu$_3$ to yield the green intermediate $(\eta^1\text{-}C_{13}H_9)Mn(CO)_3(PBu_3)_2$, which was associated with an IR band at $\nu_{CO} \approx 1850$ cm^{-1} and with ^{13}C NMR peaks that could reasonably be attributed to a $\eta^1\text{-}C_{13}H_9$ moiety. Loss of two CO groups from this intermediate would result in the postulated final product.

We have reinvestigated the reaction of I with alkylphosphines, originally with the aim of isolating $(\eta^1\text{-}C_{13}H_9)Mn(CO)_3L_2$ (L = alkylphosphine) species similar to the intermediate reported by Ji. Our observations indicate that the reaction of I with alkylphosphines does indeed produce η^1-fluorenyl complexes but that the green species observed by Ji is actually a decomposition product of the true η^1-fluorenyl complex. We have isolated and characterized $(\eta^1\text{-}C_{13}H_9)Mn(CO)_3L_2$ (IIIb, L = PEt$_3$), which we believe is the first well-characterized example of a η^1-fluorenyl complex with a transition metal. IIIb is a thermally labile complex that loses the fluorenyl moiety to form species analogous to those reported by Ji. In addition, we have found that a more efficient route to the formation of III involves the reaction of phosphines with $(\eta^6\text{-}C_{13}H_9)Mn(CO)_3$ (VI) via a novel $\eta^6 \rightarrow \eta^1$ slippage reaction.

Results and Discussion

In most of the studies described here, PEt$_3$ was used rather than PBu$_3$, primarily because PEt$_3$ was spectroscopically simpler in ^1H NMR spectra; on the basis of preliminary experiments, we concluded that the reactions of I with PEt$_3$ and PBu$_3$ were essentially identical, as expected on the basis of the similarities in their cone angles and electronic parameters (PEt$_3$, $\theta = 132°$, $\nu = 2062$ cm^{-1}; PBu$_3$, $\theta = 132°$, $\nu = 2060$ cm^{-1}).[5] When I was reacted with PEt$_3$ at high concentrations (typically 1–1.5 M) in refluxing xylene or decalin, the same changes reported by Ji[4] were observed, with a one-to-one correspondence between the species reported by Ji for L = PBu$_3$ and those observed by us for L = PEt$_3$: there was rapid buildup of a green intermediate (IVb, L = PEt$_3$; $\nu_{CO} = 1852$ cm^{-1}) followed by slow formation of a yellow final product (Vb, L = PEt$_3$; $\nu_{CO} = 1892$ cm^{-1} in xylene, 1898 cm^{-1} in decalin). Our attempts to isolate IVb proved unsuccessful.

However, we came to suspect the assignment by Ji of the final product, V, as $(\eta^5\text{-}C_{13}H_9)MnCO(PBu_3)_2$ because of its anomalously high value of $\nu_{CO} = 1898$ cm^{-1}, which is only 7 cm^{-1} lower than the average value of $\bar{\nu}_{CO} = 1905$ cm^{-1} for IIa, $(\eta^5\text{-}C_{13}H_9)Mn(CO)_2L$.[4] In comparison, for I, the weighted average carbonyl stretching frequency is $\bar{\nu}_{CO} = 1971$ cm^{-1} (hexane);[6] thus, replacement of one CO by PBu$_3$ leads to a 66-cm^{-1} shift in $\bar{\nu}_{CO}$. Connelly and Kitchen[7] reported $\nu_{CO} = 1815$ cm^{-1} (CH$_2$Cl$_2$) for $(\eta^5\text{-}C_5H_4CH_3)$-MnCO(PMePh$_2$)$_2$. The electronic parameters for PBu$_3$ and PMePh$_2$ (2060 and 2067 cm^{-1}, respectively)[5] are similar, and our own observation is that ν_{CO} values for cyclo-

pentadienyl, indenyl, and fluorenyl complexes are very similar. Thus, even when the influence of solvent was taken into account (CH$_2$Cl$_2$ typically lowers ν_{CO} by ca. 25 cm^{-1} compared to the signal in saturated hydrocarbons), it seemed unlikely that a complex of formula $(\eta^5\text{-}C_{13}H_9)$-MnCO(L)$_2$ (L = alkylphosphine) could have $\nu_{CO} = 1898$ cm^{-1}.

Addition of hexane to a green reaction mixture of I and PEt$_3$ in xylene led to precipitation of a white solid, which was identified by ^1H NMR spectroscopy and mass spectrometry as 9,9'-bifluorene. Most significantly, the ^{13}C NMR spectrum of 9,9'-bifluorene is the same as that observed by Ji for the green reaction mixture and attributed to $(\eta^1\text{-}C_{13}H_9)Mn(CO)_3(PBu_3)_2$, indicating that the fluorenyl moiety was detached from the Mn complex when the green intermediate was observed.

Identification of $(\eta^1\text{-}C_{13}H_9)Mn(CO)_3(PEt_3)_2$ and Its Decomposition Products. When I was reacted with PEt$_3$ in toluene or benzene at $T \leq 100$ °C, both IR and NMR studies showed an additional species, IIIb, which we identified as $(\eta^1\text{-}C_{13}H_9)Mn(CO)_3(PEt_3)_2$, presumably formed via an unobserved η^3 intermediate. Most characteristic was a doublet of doublets (1 H) in the ^1H NMR spectrum centered at 4.4 ppm ($J_{PH} = 6.6, 9.9$ Hz) corresponding to the single five-membered-ring proton of the fluorenyl moiety coupled to two inequivalent P atoms. The infrared spectrum showed three peaks (weak, strong, and medium intensity ratios) consistent with a tricarbonyl species.

Continued heating of the reaction mixture containing IIIb led to a decline in both the NMR and IR bands associated with it. As IIIb disappeared, formation of both fluorene and bifluorene was evident by ^1H NMR spectroscopy, with bifluorene formation predominant when IIIb was decomposing rapidly and fluorene formation more significant at lower temperatures and in the later stages of a reaction. Accompanying the appearance of bifluorene and fluorene was the formation of a green species with $\nu_{CO} = 1852$ cm^{-1}, associated with a broad, featureless ^1H NMR resonance at $\delta = -1$. The observation of both fluorene and bifluorene is consistent with a homolytic cleavage of the Mn–C bond, yielding fluorenyl radicals that would either dimerize to form bifluorene or abstract H (vide infra) to yield fluorene, depending on the rate of radical production. Loss of fluorenyl radical from IIIb yielded Mn(CO)$_3$L$_2$· (IVb, L = PEt$_3$), a 17-electron manganese radical species identified on the basis of work by Brown and co-workers,[8] in which Mn(CO)$_3$L$_2$· (L = PBu$_3$) was observed as a persistent green species (ν_{CO} (hexane) = 1860 (sh), 1855 (s)) in photolysis mixtures of Mn$_2$(CO)$_8$(PBu$_3$)$_2$ with PBu$_3$. We note further that Crocker and co-workers[9] have recently isolated and structurally characterized an analogous rhenium complex, Re(CO)$_3$L$_2$· (L = P(C$_6$H$_{11}$)$_3$), which appears to be very similar (ν_{CO} (benzene) = 1849 cm^{-1}).

Further heating of the reaction mixture containing IVb led to the slow formation of a yellow final product, Vb ($\nu_{CO} = 1892$ cm^{-1}), associated with the development of a 1:2:1 triplet ($J_{PH} = 31$ Hz) at $\delta = -8.5$ in the ^1H NMR spectrum. Brown and co-workers[8] reported that HMn(CO)$_3$L$_2$ (L = PBu$_3$; IR ν_{CO} (heptane) = 1896 cm^{-1} and ^1H NMr $\delta = -8.76$ (t, $J_{PH} = 33$ Hz)) is formed as the ultimate product in the reaction of Mn$_2$(CO)$_8$L$_2$ with L in xylene. On the basis of Brown's work, we assign Vb as the analogous triethyl-
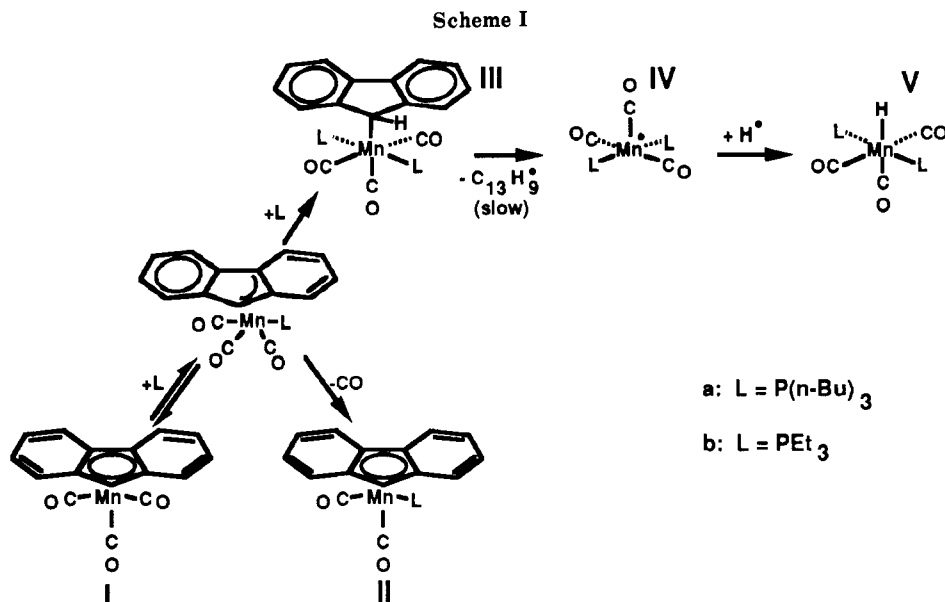
(5) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

(6) Treichel, P. M.; Johnson, J. W. *Inorg. Chem.* **1977**, *16*, 749–753.

(7) Connelly, N. G.; Kitchen, M. D. *J. Chem. Soc., Dalton Trans.* **1977**, 931–937.

(8) (a) Kidd, K. R.; Cheng. C. P.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4103–4107. (b) McCullen, S. B.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 7496–7500.

(9) Crocker, L. S.; Heinke, D. M.; Schulte, G. K. *J. Am. Chem. Soc.* **1989**, *111*, 405–406.

Scheme I

a: L = P(n-Bu)₃

b: L = PEt₃

phosphine complex HMn(CO)₃(PEt₃)₂. Altogether, we propose the mechanism presented in Scheme I to account for our observations.

Formation of both fluorene and HMn(CO)₃L₂ in these systems requires the presence of hydrogen atom donors. In the photochemical studies of Mn₂(CO)₁₀ with L = PBu₃, Brown[8a] proposed that formation of HMn(CO)₃L₂ resulted from abstraction of H atoms by Mn(CO)₃L₂• from solvent impurities. However, it seems that the possibility that excess alkylphosphine was serving as a hydrogen atom source was not considered. When we carried out the reaction of I with PEt₃ in toluene-d_8 at 100 °C, we did not observe incorporation of deuterium into either the fluorene or HMn(CO)₃(PEt₃)₂, on the basis of NMR studies.

Isolation and Properties of (η¹-C₁₃H₉)Mn(CO)₃-(PEt₃)₂. Our observations indicated that, at high PEt₃ concentrations, the reaction of I to yield IIIb proceeded even around room temperature with minimal decomposition to IVb. Reaction of I with PEt₃ (20% by volume) in benzene at 37 °C for 2 days led to nearly quantitative formation of IIIb by ¹H NMR spectroscopy. Removal of solvent and excess PEt₃ under vacuum, followed by recrystallization from hexane, yielded a pale orange-yellow solid in 44% yield. This solid was fully characterized by IR and ¹H, ¹³C, and ³¹P NMR spectroscopies and elemental analysis. The spectroscopic data for the isolated material were essentially identical with those observed in the reaction mixture, except for small shifts due to solvent effects.

On the basis of IR and ¹H NMR data, all of which indicated inequivalent phosphines, either a trans-meridional (one CO trans to the fluorenyl) or cis-meridional (all CO ligands cis to the fluorenyl) isomer would be possible. However, in the ¹³C NMR spectrum, the resonance for the C(9) carbon of the fluorenyl group is a 1:2:1 triplet (J_{PC} = 8.4 Hz) at δ = 28.3. We could find no literature information for ¹³C NMR coupling constants of directly analogous model complexes, i.e., cis and trans $^2J_{PC}$ through Mn involving sp³ C, but the general trend is for the magnitude of trans couplings to be greater than those for cis coupling by at least a factor of 2.[10] The apparent equivalence of the two J_{PC} couplings suggests that both phosphines are

cis to the fluorenyl, consistent with IIIb being the trans-meridional isomer. However, we recognize that we cannot unequivocally rule out the cis-meridional isomer. Because of steric interactions of the triethylphosphines with each other and with the fluorenyl moiety, the C(fluorenyl)–Mn–P bond angles in a cis-meridional complex would certainly be distorted from 90 and 180°; thus, predictions about the relative magnitudes of coupling constants may not be reliable.

For the trans-meridional interpretation to be consistent with the NMR data, the fluorenyl group would have to be asymmetrically displaced with respect to the two triethylphosphines. On the basis of models, we found that when the fluorenyl group was displaced symmetrically between the two phosphines, the hydrogens on C(1) and C(8) were directed into the regions occupied by the methylene groups of the phosphines. In contrast, the steric interactions between the fluorenyl group and the phosphines were minimized when the fluorenyl group resided over one of the phosphines; the aproximately tetrahedral bond angle at C(9) allowed the fluorenyl group to clear the underlying triethylphosphine group. The steric interactions hinder rotation about the Mn–C(fluorenyl) bond, accounting for the room-temperature NMR observations of inequivalent triethylphosphine groups and inequivalent phosphorus couplings to the C(9) proton. In principle, a variable-temperature NMR study might help to distinguish between a trans-meridional isomer with hindered rotation (phosphine signals would coalesce at elevated temperatures) and a cis-meridional isomer (phosphine signals would remain inequivalent). Unfortunately, heating isolated IIIb in benzene-d_6 led to decomposition, primarily to the radical species IVb; such thermal decomposition rendered impractical any variable-temperature studies.

Both the structural isomer and the Mn–C(fluorenyl) homolysis decomposition mode observed for IIIb are in contrast to those reported by Casey and co-worders[11] for η¹-cyclopentadienyl Re, W, and Mo complexes and η¹-indenyl Re complexes, which were always observed as facial

---

(10) (a) Jameson, C. L. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; Vol. 8, Chapter 6. (b) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135–213.

(11) (a) Casey, C. P.; Jones, W. D. *J. Am. Chem. Soc.* **1980**, *102*, 6154–6156. (b) Casey, C. P.; Jones, W. D.; Harsy, S. G. *J. Organomet. Chem.* **1981**, *206*, C38–C42. (c) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Jones, W. D.; Harsy, S. G. *J. Mol. Catal.* **1981**, *13*, 43–59. (d) Casey, C. P.; O'Connor, J. M.; Jones, W. D.; Haller, K. J. *Organometallics* **1983**, *2*, 535–538. (e) Casey, C. P.; O'Connor, J. M.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 1241–1246. (f) Casey, C. P.; O'Connor, J. M. *Organometallics* **1985**, *4*, 384–388.

Scheme II
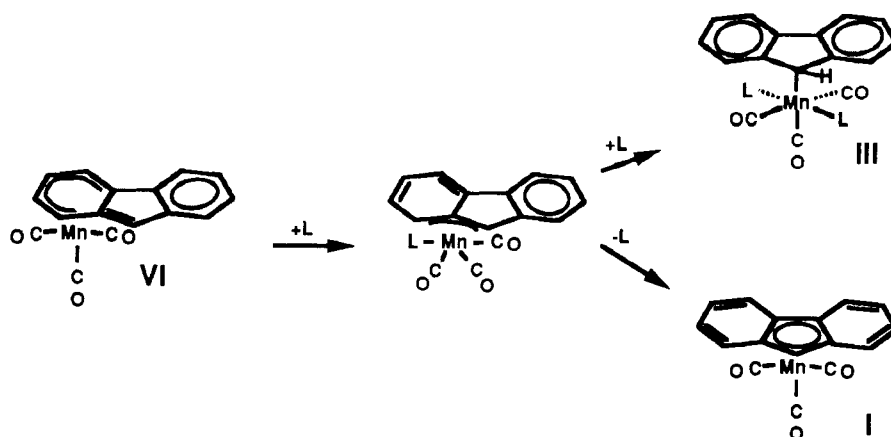
isomers with cis phosphine ligands, even for $(\eta^1$-$C_9H_7)$-$Re(CO)_3(PBu_3)_2$.[11f] The η^1-cyclopentadienyl complexes[11a-e] (L = PMe_3) $(\eta^1$-$C_5H_5)Re(CO)_3L_2$, $(\eta^1$-$C_5H_5)Re(NO)(CO)$-$(CH_3)L_2$, and $(\eta^1$-$C_5H_5)M(NO)(CO)_2L_2$ (M = W, Mo) generally lost either both phosphine ligands or one phosphine and one CO to yield η^5-cyclopentadienyl products. $(\eta^1$-$C_5H_5)Re(NO)(CH_3)(PMe_3)_3$, in the presence of high concentrations of PMe_3 in THF, produced small yields of an ionic product, $[Re(NO)(CH_3)(PMe_3)_4]^+[C_5H_5]^-$, a product of the apparently heterolytic cleavage of the Re–C(Cp) bond.[11e] The η^1-indenyl complexes[11f] $(\eta^1$-$C_9H_7)Re$-$(CO)_3L_2$ (L = PMe_3 and L_2 = bipyridyl) were reported to be stable. The differences in reactivity between IIIb and the other examples cited probably reflect differences in the metal–carbon bond strengths and also the enhanced resonance stabilization of the fluorenyl radical compared to cyclopentadienyl and indenyl radicals.

Formation of IIIb from $(\eta^6$-$C_{13}H_9)Mn(CO)_3$. We have also found that the η^6-fluorenyl complex $(\eta^6$-$C_{13}H_9)Mn$-$(CO)_3$ (VI) reacts readily with PEt_3 to yield IIIb. Indeed, this $\eta^6 \rightarrow \eta^1$ conversion appears to be much more facile than the corresponding $\eta^5 \rightarrow \eta^1$ conversion, since the reactions of VI with PEt_3 proceed readily even below room temperature with use of smaller concentrations of PEt_3.

Additional studies of the reaction of VI are currently in progress, but the following points are worth noting. First, the $\eta^6 \rightarrow \eta^1$ conversion can be driven by ligands that do not appear to drive the corresponding $\eta^5 \rightarrow \eta^1$ conversion; preliminary NMR evidence indicates formation of $(\eta^1$-$C_{13}H_9)Mn(CO)_3L_2$ with L = phosphites or arylphosphines, ligands that do not appear to form significant amounts of η^1-fluorenyl complexes with I. Second, we have found that, at 25 °C, low concentrations of PEt_3 (0.01 M) cleanly catalyze the isomerization of VI to I, without the formation of either $(\eta^5$-$C_{13}H_9)Mn(CO)_2PEt_3$[4] or $(\eta^6$-$C_{13}H_9)Mn$-$(CO)_2PEt_3$.[12] This suggests that the $\eta^6 \rightarrow \eta^1$ conversion involves the mechanism shown in Scheme II, in which attack of L on VI leads to a η^3 intermediate that can either be trapped by another L to yield III or lose L to yield I. There is both theoretical[13] and experimental[12] evidence that the uncatalyzed thermal isomerization of VI to I proceeds via an allylic intermediate with its η^3 unit spanning portions of both the five- and six-membered rings. A similar ligand-stabilized intermediate is attractive here, since it would account for both the formation of III and the isomerization.

Reactions of I and VI with PBu_3. The reaction of

PBu_3 with either I or VI led to the formation of $(\eta^1$-$C_{13}H_9)Mn(CO)_3(PBu_3)_2$ (IIIa) on the basis of IR and ^1H NMR studies; the key spectral properties of IIIa and IIIb are essentially the same. However, the much lower volatility of PBu_3 compared to that of PEt_3 made removal of excess ligand impractical; thus, attempts to isolate IIIa by use of the same approach as for IIIb were unsuccessful. Attempts to separate IIIa from excess phosphine by acid extraction or by column chromatography accelerated decomposition. The high solubility imparted by the six *n*-butyl groups prevented recrystallization of the product.

Experimental Section

General Considerations. All weighings and similar operations were carried out under an argon atmosphere in a Vacuum Atmospheres drybox, and all reactions were carried out under argon with use of cannula and Schlenk line techniques. Hexane, benzene, toluene, and xylene were dried over Na or K. $(\eta^5$-$C_{13}H_9)Mn(CO)_3$ and $(\eta^6$-$C_{13}H_9)Mn(CO)_3$ were prepared according to the method of Treichel and Johnson.[6] NMR solvents were obtained from Aldrich. PEt_3 and PBu_3 (Aldrich) were distilled. Elemental analyses were performed by Atlantic Microlabs (Norcross, GA). All NMR spectra were recorded at ambient temperature with use of an IBM NR/300AF spectrometer (300.13 MHz for ^1H). IR spectra were recorded on a Nicolet 5SXB spectrophotometer using either NaCl or CaF_2 solution cells. Mass spectral data were obtained with use of an HP5992B GC/MS instrument.

Initial Studies. A solution of 500 mg (1.64 mmol) of I and 0.80 g (6.8 mmol) of PEt_3 in 25 mL of *o*-xylene was heated at reflux for 2.5 h; an infrared spectrum of the green reaction mixture indicated that I had been entirely consumed and that the principal species had IR bands at ν_{CO} = 1892 and 1852 cm^{-1}. Adding 15 mL of hexane and cooling to -15 °C led to precipitation of a white solid (bifluorene), which was separated by decantation and recrystallized. $^{13}C\{^1H\}$ NMR (CDCl$_3$): δ 144.7, 141.6, 127.3, 126.7, 124.9, 119.6, 49.9. Mass spectrometry (*m/e* (percent relative intensity)): 330 (5.5) [M$^+$], 166 (14.4), 165 (100), 164 (6.5), 163 (5.8), 139 (3.7), 115 (2.2).

Reaction of I with PEt_3. Infrared Studies. In a typical experiment, 115 mg (0.38 mmol) of I, 0.40 g (3.6 mmol) of PEt_3, and 3.0 mL of toluene were combined in a small reaction vessel. The mixture was heated to reflux, and samples were periodically removed by syringe for IR analysis. IR (ν_{CO}, toluene) showed the rapid, sequential development of two species: IIIb, 1997 (w), 1912 (s), 1882 (m) cm^{-1}; IVb, 1852 cm^{-1}. After 45 min, the solution was deep green, and IVb was the predominant species present.

NMR Studies. In a typical experiment, 30 mg (0.10 mmol) of I, 100 mg (0.85 mmol) of PEt_3, and 0.5 mL of benzene-d_6 were combined in a septum-sealed NMR tube. The tube was heated in a constant-temperature bath at 70 °C; the tube was periodically removed from the constant-temperature bath, and spectra were recorded at room temperature. ^1H NMR for IIIb: δ 8.0–7.2 (four resonances, 2 H each, six-membered-ring protons), 4.39 (1 H, dd,

(12) Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 647–649.

(13) Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396–3411.

J_{PH} = 6.6, 9.9 Hz), 1.83 (6 H, m) and 0.51 (9 H, m) (bound PEt₃), 1.0 and 0.9 (inferred from decoupling experiments). ¹H NMR for IVb: δ –1 (broad). Resonances corresponding to fluorene and bifluorene were also observed.

In a similar procedure carried out in toluene-d_8, the reaction was continued for 6 days at 100 °C. In addition to the resonances observed for fluorene, bifluorene, IIIb, and IVb, the hydride resonance of Vb was also observed at δ –8.54 (t, J_{PH} = 31 Hz). Integrations indicated that the fluorene plus bifluorene observed accounted for greater than 95% of the initial I and that the hydride peak accounted for greater than 65% of I; at this point, some IVb was still present, and some decomposition was evident.

Isolation of (η¹-C₁₃H₉)Mn(CO)₃(PEt₃)₂. Typically, 0.25 g (2.1 mmol) of PEt₃ was added to a partially dissolved suspension of 100 mg (0.33 mmol) of I or VI in 2 mL of hexane. Reactions starting with I were carried out for approximately 24 h at 37 °C and those starting with VI for 45 min at room temperature. After the reaction was stopped, solvent and excess PEt₃ were pumped off, and the resulting product was recrystallized from hexane. Typical isolated yields for either method were 40–45%. All NMR data are for benzene-d_6. ¹H NMR (δ): six-membered-ring protons, 7.98 (2 H, d, 7.4 Hz), 7.96 (2 H, d, 7.5 Hz), 7.43 (2 H, t, 7.4 Hz), 7.31 (2 H, t, 7.3 Hz); five-membered-ring proton, 4.49 (1 H, dd, 6.8, 9.5 Hz); bound PEt₃ protons, 1.82 (6 H, m), 0.95 (15 H, overlapping multiplets), 0.54 (9 H, m). ¹³C{¹H} NMR (δ): CO carbons, 223 (broad, weak, asymmetric); quaternary carbons, 158.5,

138.8; arene carbons, 124.6, 123.6, 122.1, 119.6; C(9), 28.3 (t, J_{PC} = 8.4 Hz); PEt₃ methylene carbons, 19.6 (d, J_{PC} = 21 Hz), 18.7 (d, J_{PC} = 21 Hz); PEt₃ methyl carbons, 7.3, 7.1. ³¹P NMR (δ): 45.3, 40.5. IR: ν_{CO} (hexane) 2000 (w), 1917 (s), 1887 (m) cm⁻¹. Anal. Found (calcd) for C₂₈H₃₉MnO₃P₂: C, 62.0 (62.2); H, 7.34 (7.27).

Observation of IIIa. The reaction of I with PBu₃ was investigated briefly by NMR spectroscopy. These studies yielded observations similar to those with PEt₃, and only key results are indicated here. ¹H NMR (ca. 15% by volume PBu₃ in benzene-d_6): resonance for the five-membered-ring proton of IIIa at δ 4.49 (dd, J_{PH} = 9.4, 6.9 Hz); resonance for the hydride proton of Va at δ –8.49 (t, J_{PH} = 31 Hz).

In attempts to synthesize IIIa from VI by use of the method for IIIb described above, IR spectra of reaction mixtures indicated nearly quantitative conversion of VI to IIIa. However, when solvent was removed, the crude yellow oil, heavily contaminated by excess PBu₃, could not be purified by recrystallization. Column chromatography (elution with hexane on a Florisil column at –15 °C) and extraction with degassed, aqueous HCl led to products heavily contaminated by fluorene. IR: ν_{CO} (hexane) 1999 (w), 1915 (s), 1888 (m) cm⁻¹.

Closed-Structure Arsinidene Complexes of 16-Electron Cyclopentadienylruthenium Carbonyl Fragments. Molecular Structures of {[CpRu(CO)]₂(μ-CO)(μ-AsR)}, R = Me and Ph

Anthony-J. DiMaio,[1a] Thomas E. Bitterwolf,[1b] and Arnold L. Rheingold*,[1a]

Departments of Chemistry, University of Delaware, Newark, Delaware 19716, and University of Idaho, Moscow, Idaho 83843

The reaction of the diphenylacetylene carbonyl-substitution product of [CpRu(CO)₂]₂, specifically, [Cp₂Ru₂(CO)₂(μ-CO)(PhCCPh)] (1) with the cyclopolyarsines *cyclo*-(AsMe)₅ and *cyclo*-(AsPh)₆ have afforded monoarsinidene (RAs) products by displacement of diphenylacetylene. These products are structurally related to the supposed structure of the cis isomer of [CpRu(CO)₂]₂ in which one μ-CO ligand has been replaced by a μ-AsR ligand to form {[CpRu(CO)]₂(μ-CO)(μ-AsR)}. The R = Me (2) and Ph (3) products obtained from 1 have been crystallographically characterized. Compound 2: orthorhombic, *Pnma*, *a* = 16.170 (4) Å, *b* = 14.658 (3) Å, *c* = 6.309 (1) Å, *V* = 1495.3 (6) Å³, *Z* = 4, *R*(*F*) = 2.84%. Compound 3: monoclinic, *P*2₁/*c*, *a* = 8.241 (3) Å, *b* = 27.930 (10) Å, *c* = 7.925 (3) Å, β = 96.64 (3)°, *V* = 1811 (1) Å³, *Z* = 4, *R*(*F*) = 3.02%. The geometry at the μ-arsinidene As atom in both structures is pyramidal, and both contain Ru–Ru bonds, whereas the overwhelming majority of known dinuclear μ-AsR structures display planar As-atom environments and are not metal–metal bonded. These structures represent the first dinuclear ruthenium–inidene structures for any of the group-15 elements and the first structural characterization of a closed-structure arsinidene complex.

Introduction

Transition-metal complexes of the "inidene" ligands, RE (E = P, As, or Sb), are known in a large variety of structural forms due to the ability of the ligand to adopt μ_2-, μ_3-, and μ_4-bridging modes. This structural adaptability has been productively used in the construction and stabilization of multinuclear complexes.[2-5]

For dinuclear complexes containing μ_2-RE ligands, two subclasses are known: type I containing 16-electron metal fragments and type II containing 15-electron metal fragments.[6a] Each of the types is further divisible into pairs

(1) (a) University of Delaware. (b) University of Idaho.

(2) Huttner, G.; Knoll, K. *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 743.

(3) Arif, A. M.; Cowley, A. H.; Norman, N. C.; Orpen, A. G.; Pakulski, M. *Organometallics* 1988, *7*, 309. Jones, R. A.; Whittlesey, B. R. *Organometallics* 1984, *3*, 469.

(4) (a) Huttner, G.; Evertz, K. *Acc. Chem. Res.* 1986, *19*, 406. (b) Huttner, G. *Pure Appl. Chem.* 1986, *58*, 585.

(5) Isoelectronic cationic inidene complexes of group-16 elements are also known, e.g., [Cp(CO)₂Mn]₂SR⁺, R = Ph[5a] and Et,[5b] and [Cp(CO)₂Mn]₂TePh2⁺.[5c] (a) Braunwarth, H.; Huttner, G.; Zsolnai, L. *Angew. Chem., Int. Ed. Engl.* 1988, *27*, 698. (b) Burckett-St. Laurent, J. C. T. R.; Caira, M. R.; English, R. B.; Haines, R. J.; Nassimbeni, L. R. *J. Chem. Soc., Dalton Trans.* 1977, 1077. (c) Huttner, G.; Schuler, S.; Zsolani, L.; Gottlieb, M.; Braunwarth, Minelli, M. *J. Organomet. Chem.* 1985, *286*, 317.