Organometallics 1986, 5, 1506-1508

Registry No. 1, 15975-90-3; 2, 15975-91-4; 3, 15975-92-5; 4 (X = Br), 50701-13-8; 5 (X = Cl), 102341-13-9; 6 (X = Cl), 50726-26-6; 7 (X = Br), 62980-43-2; 8 (X = Cl), 102286-21-5; 9 (X = Cl), 99630-91-8; 10 (X = Br), 102286-22-6; 11 (X = Cl), 102306-93-4; 12 (X = Cl), 102286-23-7; 13, 102286-24-8; 14, 102286-25-9.

Supplementary Material Available: Crystallographic data for 1, tables of atomic coordinates, bond lengths, bond angles, and observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Electron Spin Resonance and Molecular Orbital Study of Binuclear Phosphido-Bridged Iron Carbonyl Radicals[†]

R. T. Baker,* P. J. Krusic,* J. C. Calabrese, and D. C. Roe

Central Research & Development Department
Experimental Station
E. I. du Pont de Nemours & Company
Wilmington, Delaware 19898

Received March 31, 1986

Summary: A new family of 33-electron, paramagnetic phosphido-bridged diiron carbonyl complexes $Fe_2(CO)_7(\mu\text{-}PR_2)$ (I, R = Et, Ph, Cy, *t*-Bu) is reported. These radical species can be isolated in analytically pure form and have been studied by IR and ESR spectroscopy. Studies with ^{13}CO indicate complete CO exchange in seconds in dilute pentane solutions, very rapid scrambling of the CO ligands on the ESR time scale, and reversible addition of a CO molecule to give the 35-electron $Fe_2(CO)_8(\mu\text{-}PR_2)$ adducts (II). Spectroscopic data and EHMO calculations support structures for I and II which differ from those determined previously for the corresponding diamagnetic anions $[Fe_2(CO)_n(\mu\text{-}PPh_2)]^-$ (n = 7, 8). Radicals I react rapidly with 1 equiv of $P(OMe)_3$ to give monosubstituted derivatives $Fe_2(CO)_6[P(OMe)_3](\mu\text{-}PR_2)$.

The cooperative effects of two transition-metal centers held together by a bridging phosphido ligand are of great interest in organometallic chemistry.[1] Such adjacent metal centers offer modes of bonding and reaction pathways which are not possible at single metal centers and which may produce enhanced activity and selectivity in homogeneous catalysis. With few exceptions,[2] the vast majority of binuclear phosphido-bridged systems studied so far have been diamagnetic. We now report the preparation, characterization, and ESR studies of a new family of paramagnetic phosphido-bridged binuclear iron carbonyl complexes $Fe_2(CO)_7(\mu\text{-}PR_2)$ (I, R = Et (A), Ph (B), cyclohexyl, *t*-Bu).

Scheme I

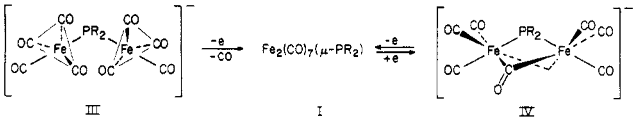


Table I. ESR Parameters for $Fe_2(CO)_7(\mu\text{-}PR_2)$ Radicals[a]

	PEt_2	PPh_2	PCy_2	P-*t*-Bu_2
g_1	2.0990	2.0978	2.0958	2.0826
g_2	2.0323	2.0309	2.0317	2.0426
g_3	2.0263	2.0259	2.0255	2.0130
g_{av}	2.0525	2.0515	2.0510	2.0461
g_{iso}	2.0526	2.0520	2.0508	2.0469
$A_1(P)$	22.1	21.5	20.6	19.0
$A_2(P)$	28.2	28.7	28.6	23.8
$A_3(P)$	20.7	20.7	19.7	21.8
$A_{av}(P)$	23.7	23.6	23.0	21.5
$A_{iso}(P)$	23.16	23.39	22.65	20.51

[a] Anisotropic parameters at −173 °C in 3-methylpentane; isotropic parameters at −70 °C in pentane. The hyperfine splittings are in gauss.

One-electron oxidation of the anions III and IV[3] with [ferrocenium][BF_4] yields the 33e binuclear radicals I, isolated as sublimable, air-sensitive, dark green crystals (Scheme I).[4] Complexes I were characterized by elemental analysis, MS, IR, and ESR spectroscopy. The IR spectra of I showed no absorption bands due to bridging carbonyls and are strikingly similar to the IR spectrum of the structurally characterized 34e complex $FeCo(CO)_7(\mu\text{-}PMe_2)$ (V).[5,6] We conclude that I and V are isostructural, with one six-coordinate, pseudooctahedral metal center and one five-coordinate, distorted trigonal-bipyramidal metal center (Scheme II).

The ESR spectra of I in dilute pentane solutions are doublets (Figure 1A), appropriate for a weak hyperfine interaction with a phosphorus atom (Table I). The pow-

---

[†] Contribution no. 3785.

(1) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163; *Pure Appl. Chem.* **1982**, *54*, 113. Carty, A. J.; Hartstock, F.; Taylor, N. J. *Inorg. Chem.* **1982**, *21*, 1349. Roberts, D. A.; Steinmetz, G. R.; Breen, M. J.; Shulman, P. M.; Morrison, E. D.; Duttera, M. R.; DeBrosse, C. W.; Whittle, R. R.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 846. Breen, M. J.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1069. Finke, R. G.; Gaughan, G.; Pierpont, C.; Cass, M. E. *Ibid.* **1981**, *103*, 1394. Finke, R. G.; Gaughan, G.; Pierpont, C.; Nordick, J. H. *Organometallics* **1983**, *2*, 1481. Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Moore, E. J.; Rose-Munch, F. *Inorg. Chem.* **1982**, *21*, 146. McKennis, J. S.; Kyba, E. P. *Organometallics* **1983**, *2*, 1249. Yu, Y.-F.; Gallucci, J.; Wojcicki, A. *J. Chem. Soc., Chem. Commun.* **1984**, 653; *J. Am. Chem. Soc.* **1983**, *105*, 4826. Jones, R. A.; Stuart A. L.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 1437. Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 319. Klingert, B.; Werner, H. *J. Organomet. Chem.* **1983**, *252*, C47. Zolk, R.; Werner, H. *Ibid.* **1983**, *252*, C53. Muller, M.; Vahrenkamp, H. *Chem. Ber.* **1983**, *116*, 2322. Braunstein, P.; Mott, D.; Fars, O.; Louer, M.; Grandjean, D.; Fischer, J.; Mitschler, A. *J. Organomet. Chem.* **1981**, *213*, 79. Seyferth, D.; Wood, T. G.; Fackler, J. P., Jr.; Mazany, A. M. *Organometallics* **1984**, *3*, 1121. Haines, R. J.; Steen, N. D. C. T.; English, R. B. *J. Chem. Soc., Dalton Trans.* **1984**, 515. Brauer, D. J.; Heitkamp, S.; Sommer, H.; Stelzer, O. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 734. Powell, J.; Gregg, M. R.; Sawyer, J. F.; *J. Chem. Soc., Chem. Commun.* **1984**, 1149. Schafer, H.; Zipfel, J.; Migula, B.; Binder, D. *Z. Anorg. Allg. Chem.* **1983**, *501*, 111. Henrick, K.; Iggo, J. A.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1984**, 209. Baker, R. T.; Tulip, T. H.; Wreford, S. S. *Inorg. Chem.* **1985**, *24*, 1379. Baker, R. T.; Tulip, T. H. *Organometallics*, in press.

(2) Dessy, R. E.; Kornmann, R.; Smith, C.; Haytor, R. *J. Am. Chem. Soc.* **1968**, *90*, 2001. Dessy, R. E.; Wieczorek, L. *Ibid.* **1969**, *91*, 4963. Dessy, R. E.; Bares, L. A. *Acc. Chem. Res.* **1972**, *5*, 415. Cowley, A. H.; Kemp. R. A.; Wilburn, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 331. Gaudiello, J. G.; Wright, T. C.; Jones, R. A.; Bard, A. J. *Ibid.* **1985**, *107*, 888. Kawamura, T.; Enoki, S.; Hayashida, S.; Yonezawa, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3417. Madach, T.; Vahrenkamp, H. *Chem. Ber.* **1981**, *114*, 513. Karsch, H. H.; Milewski-Mahrla, B. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 814.

(3) Osterloh, W. T. Ph.D. Thesis, 1982, University of Texas, Austin, TX; Univ. Microfilms Intern., Ann Arbor, MI.

(4) In a typical preparation, a solution of 956 mg (4.32 mmol) of PPh_2Cl in 50 mL of THF was added dropwise to a suspension of 1.65 g (4.32 mmol) of $Na_2Fe_2(CO)_8$ in 100 mL of THF over 30 min. After being stirred for 1 h, the solution was concentrated in vacuo to 20 mL and filtered through Celite and the solvent evaporated. The residue was washed with 2 × 15 mL of hexane and dissolved in 50 mL of CH_2Cl_2, and a solution of 1.18 g (4.32 mmmol) of $[Cp_2Fe][BF_4]$ in 50 mL of CH_2Cl_2 was added dropwise over 30 min. The resulting dark green solution was stirred for 18 h and evaporated to dryness. Extraction of the residue with 250 mL of hexane and cooling to −30 °C for 14 h afforded 1.60 g of green-black crystals of $Fe_2(CO)_7(\mu\text{-}PPh_2)$ (75%), mp 90–93 °C. Anal. Calcd for $C_{19}H_{10}Fe_2O_7P$: C, 46.29; H, 2.04; Fe, 22.66; P, 6.28. Found: C, 46.24, 46.00; H, 2.21, 2.14; Fe, 22.7, 22.8; P, 6.14, 6.16.

(5) IR for IA in hexane: 2029 (m), 1994 (m), 1978.5 (vs), 1958 (s), 1950 (s, sh), 1922.5 (s), 1908 (s) cm^{-1}.

(6) Keller, E.; Vahrenkamp, H. *Chem. Ber.* **1977**, *110*, 430. Benson, B. C.; Jackson, R.; Joshi, K. K.; Thompson, D. T. *J. Chem. Soc., Chem. Commun.* **1968**, 1506.

0276-7333/86/2305-1506$01.50/0

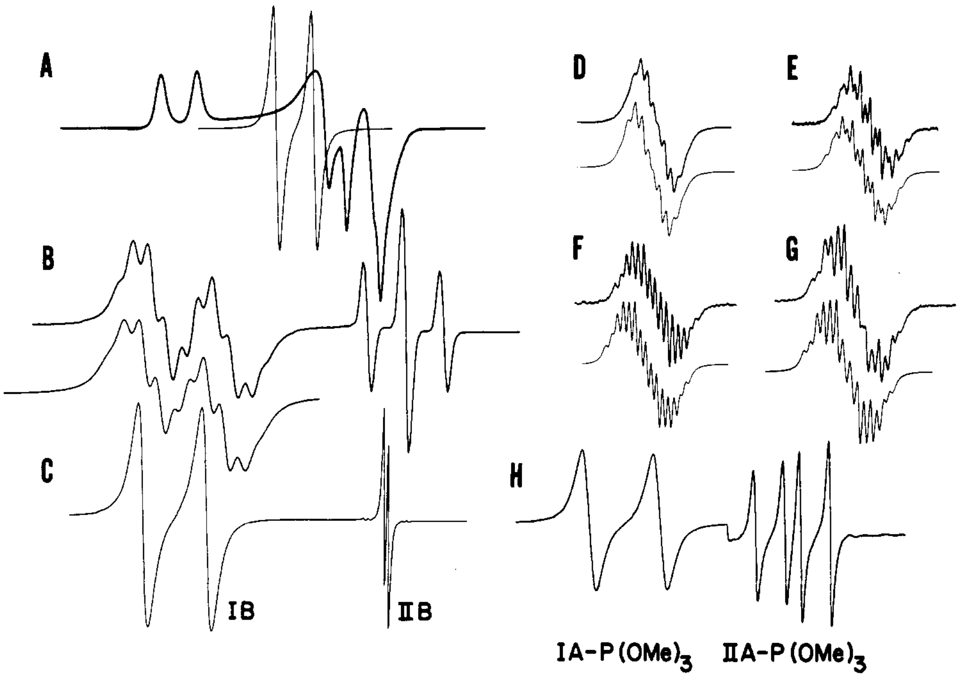


Figure 1. (A) ESR spectrum of $Fe_2(CO)_7(\mu\text{-}PEt_2)$ in pentane at -70 °C (thin line) and in 3-methylpentane at -173 °C (heavy line). (B) ESR spectrum (-80 °C) obtained by bubbling ^{13}CO through a pentane solution of $Fe_2(CO)_7(\mu\text{-}PPh_2)$. (C) ESR spectrum (-70 °C) obtained by bubbling CO through the same solution. (Note ^{13}C satellite lines for IIB.) (D) Expansion of the central line of the triplet in Figure 1B at -30 °C. (E) At -70 °C. (F) At -90 °C. (G) At -110 °C and computer simulations. (H) ESR spectrum (-60 °C) obtained by bubbling CO through a pentane solution of $Fe_2(CO)_6[P(OMe)_3](\mu\text{-}PEt_2)$ (the step in the base line is due to a change of gain).

der spectra in 3-methylpentane (Figure 1A) show three principal values of the **g** tensor with nearly isotropic ^{31}P splittings (Table I). Pentane solutions of IA are thermochromic (dark brown below -50 °C, light green at 25 °C), and the ESR signal intensity decreases reversibly on cooling. Furthermore, pure crystals of IA give no ESR spectrum. This behavior indicates association of the binuclear radicals to give diamagnetic clusters. The other derivatives studied have bulkier PR_2 bridges and show no appreciable tendency to associate.

The powder ESR spectra of I are remarkably similar to those of trigonal bipyramidal $(CO)_4Fe[C(O)R]$ radicals,[7] suggesting that the unpaired electron is localized on the five-coordinate Fe center. Using the atomic coordinates of the diamagnetic analogue V, we carried out EHMO calculations on the model $Fe_2(CO)_7(\mu\text{-}PH_2)$ complex (*d*(PH) = 1.46 Å). It was found that the SOMO is indeed largely localized on the $Fe(CO)_3$ fragment (91.6%) with only minor contributions from the PH_2 (0.8%) and the $Fe(CO)_4$ (7.7%) fragments. In the $Fe(CO)_3$ fragment, 39.3% of the unpaired electron density resides on the Fe center, 50.5% on the two equatorial CO ligands, and only 1.8% on the axial CO ligand trans to the bridging P atom.[8]

According to these calculations, one would expect two strongly interacting ^{13}C nuclei in the ^{13}C-labeled radicals. To test this prediction, we prepared I-^{13}*CO* by bubbling ^{13}CO (99%) through pentane solutions of I. Infrared monitoring showed that *complete CO exchange occurred in seconds.* The ESR spectrum of IB-^{13}*CO* at -80 °C showed additional hyperfine structure which was simulated by using five equivalent ^{13}C atoms (5.9 G, Figure 1B). The observation of five equivalent ^{13}C atoms is presumably the result of a fluxional process which interconverts, on the ESR time scale, the equatorial CO ligands on both Fe centers (labeled 1–5 in I), but *not* the axial CO's trans to the PR_2 bridge (Scheme II). The observed ^{13}C splitting would then be the average of relatively large ^{13}C couplings in sites 1 and 2 and very small couplings in sites 3–5 of structure I.[9] This exchange presumably proceeds through a CO-bridged transition-state structure analogous to the structure of anion IV which is also fluxional on the NMR time scale.[3] No resolvable ^{13}C hyperfine structure was observed for the two axial CO's trans to the PR_2 bridge, in agreement with the EHMO calculations.

In the CO exchange reactions of I, a new species II is observed by ESR at higher magnetic fields. With natural-abundance CO, the spectrum of IIB (Figure 1C) consists of a doublet of exceptionally narrow line width (0.8 G) due to a very weak ^{31}P hyperfine interaction (1.73 G, g = 2.0043, -70 °C).[10] With ^{13}CO (99%), this spectrum is replaced by a triplet of broader line width (Figure 1B) and a substantial splitting (14.04 G, temperature independent), indicating two strongly interacting, equivalent ^{13}C nuclei. Under conditions of high resolution, each component of this triplet shows additional hyperfine structure which can be simulated in terms of temperature-dependent hyperfine interactions with one phosphorus and groups of four equivalent and two equivalent ^{13}C atoms (e.g., 1.730 G (1 P), 0.859G (4 C), 0.500 G (2 C) at -70 °C, Figure 1E).[11] The new species are the 35e radicals $Fe_2(CO)_8$ (μ-PR_2) (II) which result by reversible CO addition to I (Scheme II). We have studied this equilibrium with a newly developed high-pressure sapphire ESR sample tube.[12] In pentane at 25 °C and 50 atm of CO, the

---

[7] Krusic, P. J.; Cote, W. J.; Grand, A. *J. Am. Chem. Soc.* **1984**, *106*, 4642.

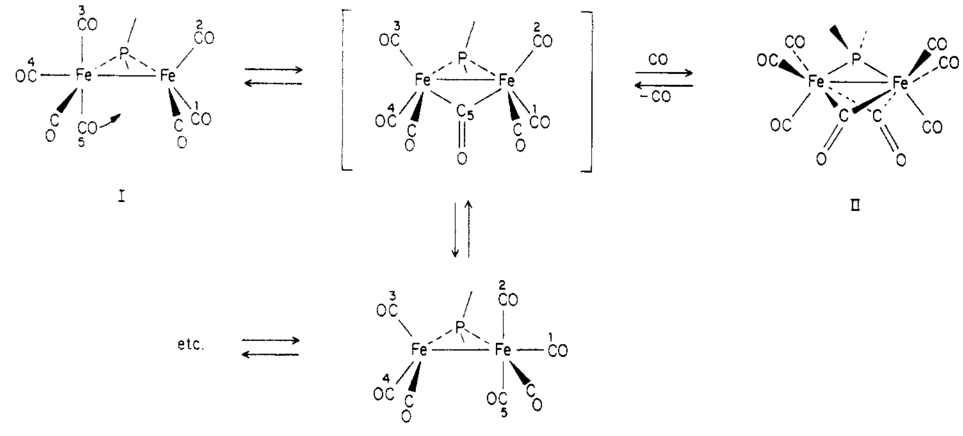
[8] The unpaired electron populations were calculated by summing the squares of the EH coefficients (×100) of the valence atomic orbitals which make up the SOMO for the different atomic groups of the molecule. When they did not add up to exactly 100, they were normalized to do so but the change was usually small (cf. ref 7). The squares of the EH coefficients for each MO and each atom (normalized to 2.0) are also found in the reduced charge matrix of the EHMO program.

[9] a) Assuming that the averaging involves three sites of zero hyperfine coupling and two equivalent sites of appreciable coupling, the ^{13}C coupling for the strongly interacting ^{13}C atoms in a static molecule would be 5.9 × 5/2 = 14.75 G. This value compares favorably with 11 G observed for the equatorial ^{13}C atoms in the trigonal-bipyramidal $(CO)_4$-$[FeC(O)R]$ radicals.[7] (b) Fluxional behavior of ^{13}CO ligands in a paramagnetic iron carbonyl cluster has been observed before. Cf. Krusic, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 2131.

[10] The g value is slightly temperature dependent, varying almost linearly from 2.0037 at -120 °C to 2.0060 at 25 °C.

[11] 1.625 G (1 P), 0.663 G (4 C), 0.500 G (2 C) at -30 °C; 1.820, 0.980, 0.500 G at -90 °C and 1.870, 1.090, 0.500 G at -110 °C.

Scheme II



ratio [IIB]/[IB] is ca. 0.03 while at −30 °C it is ca. 0.3.

The ESR parameters strongly suggest a symmetric structure for II as shown in Scheme II in which substantial unpaired electron density resides on a pair of equivalent CO ligands. The SOMO in these radicals must have a very small Fe character to account for the narrow line width and a *g* factor close to the "free-spin" value which are more characteristic of organic than metal-centered radicals. Indeed, EHMO calculations on the model compound $Fe_2(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PH_2)$[13] show insignificant unpaired electron density on the two Fe centers (0.2%) and a very substantial one (67.6%) on the two *bridging* CO ligands. The remaining unpaired electron densities are 0.2% for the PH_2 group and 31.7% and 0.4%, respectively, for the four cis and two trans terminal CO ligands, in qualitative agreement with the ESR data.[15]

The very rapid CO exchange indicates high substitutional lability for radicals I. Indeed, they react at room temperature with 1 equiv of $P(OMe)_3$ to give isolable, monosubstituted derivatives $Fe_2(CO)_6[P(OMe)_3](\mu\text{-}PR_2)$ (I-$P(OMe)_3$).[16] The ESR spectrum of IA-$P(OMe)_3$ in pentane is quite similar to that of its precursor IA and shows no resolvable hyperfine splitting due to the $P(OMe)_3$ ligand ($a(^{31}P) = 21.77$ G, $g = 2.0507$, −60 °C).[19] Evidently, the "invisible" phosphite ligand occupies one of the two positions trans to the bridging PR_2 group where the ^{13}CO ligands were also invisible. However, under a CO atmosphere, a new resonance appears at higher field (Figure 1H) due to $Fe_2(CO)_7[P(OMe)_3](\mu\text{-}PEt_2)$[IIA-$P(OMe)_3$] which clearly shows coupling to two ^{31}P atoms (8.84 G, 13.66 G, $g = 2.0186$). Under ^{13}CO, the upfield resonance becomes very complicated and the spectrum of IA-$P(OMe)_3$ acquires additional structure due to five equivalent ^{13}C atoms (cf. Figure 1B). The latter observation is consistent with the phosphite ligand being trans to the PR_2 bridging group where it does not interfere with the fluxional behavior of the five equatorial CO ligands.

The details of this work and our investigations of the chemical properties (substitution chemistry, photochemical activation of H_2, etc.) and catalytic activity[20] of these paramagnetic complexes will be reported elsewhere.

Acknowledgment. We thank Professor E. P. Kyba for communicating to us Dr. Osterloh's thesis work prior to publication and for providing samples of $[Et_4N][Fe_2(CO)_n(\mu\text{-}PPh_2)]$ (n = 7, 8). We also acknowledge the fine technical assistance of D. J. Jones (ESR) and S. A. Hill (IR, synthesis).

Registry No. I (R = Cy), 102211-01-8; I (R = *t*-Bu), 102211-02-9; IA, 102210-99-1; IB, 102211-00-7; II (R = Cy), 102211-05-2; II (R = *t*-Bu), 102211-06-3; IIA, 102211-03-0; IIA-$P(OMe)_3$, 102211-17-6; IIB, 102211-04-1; III (R = Cy), 102211-09-6; III (R = *t*-Bu), 102211-10-9; IIIA, 102211-07-4; IIIB, 102211-08-5; IV (R = Cy), 102211-13-2; IV (R = *t*-Bu), 102211-14-3; IVA, 102211-11-0; IVB, 102211-12-1; $Fe_2(CO)_7(\mu\text{-}PH_2)$, 102211-15-4; $(CO)_6Fe_2(\mu\text{-}CO)_2(\mu\text{-}PH_2)$, 102211-16-5.

---

(12) Roe, D. C. *J. Magn. Reson.* **1985**, *63*, 388. Krusic, P. J.; Jones, D. J.; Roe, D. C. *Organometallics* **1986**, *5*, 456.

(13) The calculations assume that the model compound has the structure of $Fe_2(CO)_9$[14] with one of the bridging CO ligands replaced by a PH_2 group [Fe–Fe = 2.523 Å; Fe–P = 2.32 Å; P–H = 1.46 Å; H–P–H = 114.5°].

(14) Cotton, F. A.; Troup, J. M. *J. Chem. Soc., Dalton Trans.* 1984, 800.

(15) The extensive delocalization of the impaired electron on the CO ligands in II is not surprising. The $Fe_2(CO)_8PR_2$ radical species are electronically analogous to $Fe_2(CO)_9$ with an added electron since a bridging PR_2 is a three-electron ligand. The unpaired electron in this hypothetical radical anion will wish to reside mostly on the ligands to maintain the desirable 18-electron count at each Fe center existing in $Fe_2(CO)_9$. Our EHMO calculations on $Fe_2(CO)_9^-$ indeed show that the SOMO in this radical anion is made up exclusively of the AO's of the CO ligands (76.4% bridging CO's; 23.6% terminal CO's). A completely analogous situation, judging by similar ESR behavior, obtains with the radical species $Fe_2(CO)_8SR$, isostructural with II, which have a three-electron thiolato group instead of the PR_2 group of II (Krusic, P. J., unpublished results).

(16) The ease of this substitution reaction is in contrast with the more severe reaction conditions needed to effect substitution with tertiary phosphines in the isostructural even-electron $(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ analogue.[17] Greatly enhanced substitutional lability has been associated with odd-electron transition-metal carbonyl systems.[18]

(17) Regragui, R.; Dixneuf, P. H.; Taylor, N. J.; Carty, A. J. *Organometallic* **1986**, *5*, 1.

(18) Cf. Brown, T. L. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 80.

(19) The powder spectra also show coupling to only one P atom: 2.0933 (g_1), 2.0325 (g_2), 2.0248 (g_3), 21.0 G (A_1), 26.4 G (A_2), 19.1 G (A_3).

(20) Menon, R.; Baker, R. T.; Krusic, P. J.; San Filippo, J., Jr., manuscript in preparation.

Preparation of Ditungsten Hexakis(2,6-dimethylphenoxide) and Its Reaction with Acetylenes To Give Tungstenacyclobutadiene Complexes

I. A. Latham, L. R. Sita, and R. R. Schrock*

Department of Chemistry, Room 6-331
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received April 14, 1986

Summary: The reaction between $W_2(O\text{-}t\text{-}Bu)_6$ and excess, fused 2,6-dimethylphenol produces $W_2(DMP)_6$ in high yield (DMP = 2,6-dimethylphenoxide). $W_2(DMP)_6$ re-