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Formation and Properties of Substituted Manganese Carbonyl Radicals[1]

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Abstract: Extended photolysis of bis(tributylphosphine)dimanganese octacarbonyl, $Mn_2(CO)_8(PBu_3)_2$, in the presence of excess PBu_3, or of tris(triethyl phosphite)dimanganese heptacarbonyl, $Mn_2(CO)_7[P(OEt)_3]_3$, in heptane, with periodic removal of CO, results in formation of paramagnetic species. The frozen solution containing $Mn_2(CO)_8(PBu_3)_2 + PBu_3$ exhibits an ESR spectrum consistent with a square-pyramidal $Mn(CO)_3(PBu_3)_2$· radical, with mutually trans PBu_3 groups in basal positions. An analogous, but less well-resolved, ESR spectrum is obtained for the frozen $Mn_2(CO)_7[P(OEt)_3]_3 + P(OEt)_3$ solution following irradiation. The radicals formed are apparently prevented from recombining by steric repulsions due to the phosphorus ligands. The $Mn(CO)_3L_2$· radicals slowly abstract hydrogen from solvents; with xylene the reaction is relatively rapid.

The substitution reactions of the group 7 dinuclear metal carbonyl compounds have been the subjects of several reports. In general, mono- or disubstitution of $Mn_2(CO)_{10}$ by a monodentate phosphorus ligand occurs in the axial[2] or 9,10 positions.[3-13] Ligands of relatively small steric requirement have been found to substitute into the equatorial positions.[14,15] There have been few reports of well-characterized dimers of the type $Mn_2(CO)_7L_3$, where L is a monodenate ligand;[8,16,17] three cases of the type $Mn_2(CO)_6(L-L)_2$ are known, in which L–L is a bidentate ligand;[18-20] for L–L = diphenylphosphinomethane, the ligands are bonded in the 1,5 and 3,7 positions.[21,22]

The relative paucity of examples of the more highly substituted derivatives of $Mn_2(CO)_{10}$ is related to the fact that the metal–metal bond is not stable. There are several reports in the literature of monomeric, paramagnetic metal carbonyl species $Mn(CO)_{5-n}L_n$· or $Mn(CO)_{5-2n}(L-L)_n$·; these prior evidences are summarized in Table I. Analogous species have been formulated for rhenium.[30,31]

While reports of the formation of substituted metal carbonyl radicals are numerous, these species have not, in general, been well characterized. In fact, current evidence suggests that in most cases, the supposed manganese(0) radical species have not been observed. It appears from relatively recent studies,[11,32] and on the basis of our own work, that, while radicals may have been formed in the systems investigated, the physical observations made were of the corresponding hydride, e.g., $Mn(CO)_{5-n}L_nH$. The only radical species for which a solid-state crystal structure determination has been carried out is $Mn(CO)(C_4H_6)_2$·.[28]

In this contribution we report the results of exhaustive photosubstitution of $Mn_2(CO)_{10}$ by either tributylphosphine, PBu_3, or triethyl phosphite, $P(OEt)_3$, including evidence for formation of moderately stable radical species.

Experimental Section

Solvents, techniques for handling of materials, and instrumentation are described in the previous paper.[17] The photochemical substitution

reactions of $Mn_2(CO)_8(PBu_3)_2$ or $Mn_2(CO)_7[P(OEt)_3]_3$ were carried out in a Pyrex solution chamber that could be attached to a vacuum line for degassing and repeated removing of CO during photolysis. The photolyses were carried out on thoroughly degassed solutions, using a 650-W GE type DVY tungsten-halogen lamp, with 3400 K temperature. The UV–visible or ESR spectra of the photolyzed solutions were recorded without opening the chamber, by transferring a portion of the solution to an attached side arm fitted with an appropriate cell. Samples for IR analysis were obtained by removal of a sample from the chamber in an inert atmosphere box, using a gas-tight syringe. The photolysis solutions proved to be extremely sensitive to traces of oxygen; only with the most diligent efforts was it possible to obtain reproducible results.

The ESR spectra were obtained on a Varian Model 9 X-band spectrometer.

The hydrides $HMn(CO)_3(PBu_3)_2$ and $HMn(CO)_3[P(OEt)_3]_2$ were formed in a thermal reaction by refluxing $Mn_2(CO)_{10}$ or the appropriate $Mn_2(CO)_8L_2$ compound plus L in reagent grade xylene at atmospheric pressure under N_2 for 80 h.[33] The hydrides were not isolated but their formulations as $HMn(CO)_3L_2$ were established in each case from the ^1H NMR spectra in benzene. The spectrum for $HMn(CO)_3(PBu_3)_2$ was centered at τ 18.76 with $J(H-P) = 33$ Hz. For $HMn(CO)_3[P(OEt)_3]_2$ the triplet is centered at τ 17.93, $J(H-P) = 43$ Hz. The IR spectrum of $HMn(CO)_3(PBu_3)_2$ exhibited a single CO stretching mode in heptane at 1896 cm^{-1}.[34] Bands were observed for $HMn(CO)_3[P(OEt)_3]_2$ at 1945 and 1924 cm^{-1}.

Results

Photolysis of $Mn_2(CO)_8(PBu_3)_2$. A heptane solution of $Mn_2(CO)_8(PBu_3)_2$, 10^{-2} M, with 2×10^{-2} M PBu_3, was irradiated with repeated degassing to remove any CO formed. Over a period of several hours the color of the solution changes from an orange to green. After continued photolysis without degassing it changes to pale yellow. The green color during the intermediate stages of the reaction results from the absorption at 355 nm due to $Mn_2(CO)_8(PBu_3)_2$, and a broad absorption at about 750 nm due to an intermediate product.

The green solution yields an ESR signal at room temperature, as shown in Figure 1. A frozen solution spectrum, taken at 83 K, is shown in Figure 2. This spectrum was simulated by
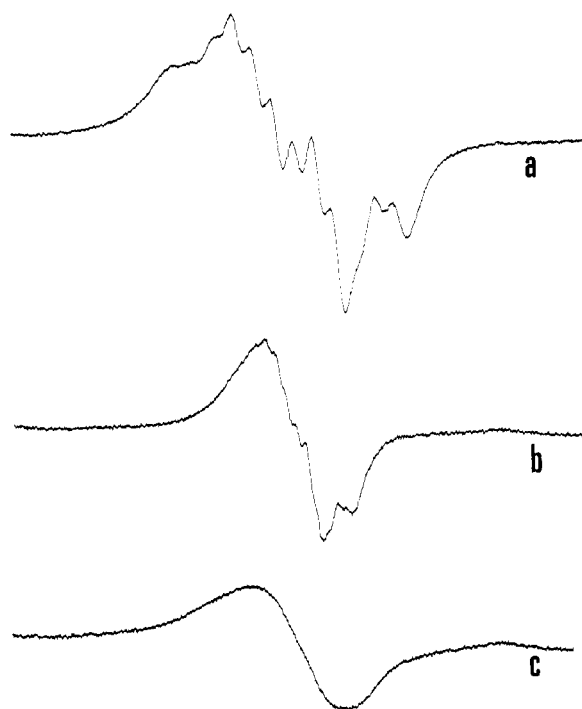
Figure 1. ESR spectra of a heptane solution of $Mn_2(CO)_8(PBu_3)_2$ and PBu_3, following photolysis, with CO removal: (a) 293 K, spectrum width 0.02 T; (b) 240 K, spectrum width 0.04 T; (c) 207 K, spectrum width 0.04 T.
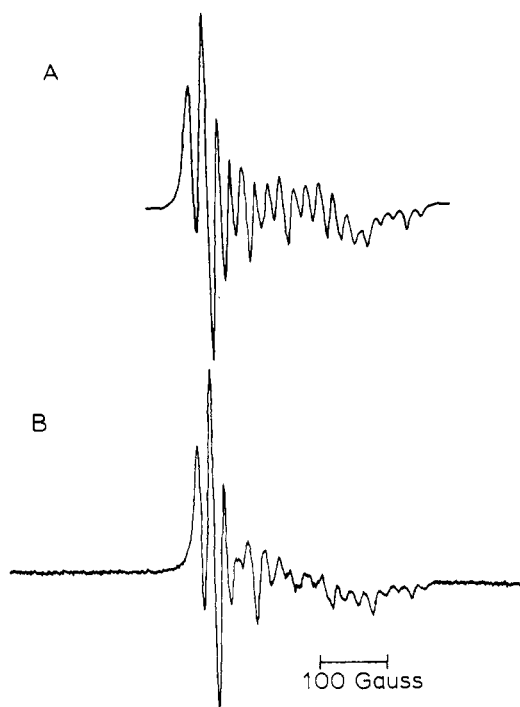
Figure 2. ESR spectrum of frozen (83 K) heptane solution of $Mn_2(CO)_8$-$(PBu_3)_2$ + PBu_3 following photolysis, with CO removal. The upper spectrum is observed; the lower is computer simulated with the parameters listed in Table II.

assuming a single paramagnetic species with a doublet ground state, an axially symmetric g tensor, and hyperfine interaction with two equivalent ^{31}P ($I = 1/2$) and a single ^{55}Mn ($I = 5/2$). The simulated spectrum is shown in Figure 2; the g values and hyperfine constants employed are listed in Table II. This table also lists the approximate values of averaged hyperfine constants and g value obtained from the room temperature ESR spectrum.

Table I. Summary of Reports of Formation of $Mn(CO)_{5-n}L_{n'}$ or $Mn(CO)_{5-2n}(L-L)_{n'}$ Radicals

Compd	Solvent	Mode of formation	Temp, °C	Ref
$Mn(CO)_4PPh_{3'}$	Xylene	Thermal	120	3, 23
$Mn(CO)_4P(C_2H_5)_{3'}$	Xylene	Thermal	120	3
$Mn(CO)_4AsPh_{3'}$	Xylene	Thermal	120	3, 23
$Mn(CO)_4SbPh_{3'}$	Xylene	Thermal	120	3
$Mn(CO)_3(PPh_3)_2 \cdot ^b$		Thermal		24–26
$Mn(CO)_3(diars) \cdot ^a$	Neat	Thermal	160	18
$Mn(CO)_3(dpe) \cdot ^a$	DME^a	Photo	25	19, 27
$Mn(CO)(dpe)_2 \cdot ^{a,c}$	DME^a	Photo	25	19, 27
$Mn(CO)(C_4H_6)_2 \cdot$		Photo	−30	28

^{a} diars = o-phenylenebisdimethylarsine; dpe = diphenylphosphinoethane; DME = dimethoxyethane. ^{b} The substance reported in ref 26 as $Mn(CO)_3(PPh_3)_2$ is almost certainly $HMn(CO)_3(PPh_3)_2$. ^{c} However, see ref 29.

Table II. ESR Parameters of $Mn(CO)_3(PBu_3)_2 \cdot$ in Heptane

| | 83 K | | 298 K |
	‖	⊥	isotropic
$A_{Mn}{}^a$	54.1	35.7	7
$A_P{}^a$	20	19	21
g	2.040	2.040	2.030

^{a} Hyperfine couplings in tesla × 10^4.

In addition to the absorptions due to $Mn_2(CO)_8(PBu_3)_2$, the IR spectrum of the green solution yields absorptions at 1912 (vw), 1896 (m), 1862 (sh), 1856 (m), and 1836 cm^{-1} (w).

After the reaction solution has turned yellow, there is no evidence for an ESR signal. Only one IR absorption at 1896 cm^{-1}, assigned to $HMn(CO)_3(PBu_3)_2$, is seen in addition to the bands of $Mn_2(CO)_8(PBu_3)_2$. The ^1H NMR spectrum of the solution is identical with that for $HMn(CO)_3(PBu_3)_2$ prepared thermally (see Experimental Section).

Photolysis of $Mn_2(CO)_7[P(OEt)_3]_3$. A heptane solution of $Mn_2(CO)_7[P(OEt)_3]_3$, $\sim10^{-2}$ M, with 10^{-2} M $P(OEt)_3$, was irradiated with repeated degassing. The color of the solution changes from yellow to a red-orange to a pale yellow. The red-orange solution yields a weak ESR signal. The ESR spectrum as a function of temperature is shown in Figure 3. The spectrum consists of a sextet of triplets, presumably the result of hyperfine interaction of the unpaired electron with two equivalent ^{31}P, isotropic coupling constant 42 G, and with a single ^{55}Mn, isotropic coupling constant 14 G, isotropic g value 2.031 ± 0.005. The intensity of the ESR signal increases with increasing temperature, to 90 °C. However, when the solution is cooled to room temperature, the signal intensity remains high; no change in intensity is noted for a period of 12 h. After several days the signal shows an intensity characteristic of the preheated solution.

The ESR spectrum of a frozen solution, at 83 K, is shown in Figure 4. No attempt was made to computer simulate this spectrum.

The pale yellow solution resulting from extended photolysis of the red-orange solution without degassing does not exhibit an ESR signal. In addition to the bands due to $Mn_2(CO)_7$-$[P(OEt)_3]_3$, two IR absorptions, at 1945 and 1924 cm^{-1}, are ascribed to $HMn(CO)_3[P(OEt)_3]_2$, by comparison with the bands seen for $HMn(CO)_3[P(OEt)_3]_2$ prepared thermally.

Discussion

When efforts are not made to remove CO from solution at intervals during photolysis, substitution of $Mn_2(CO)_{10}$ beyond $Mn_2(CO)_8(PBu_3)_2$ or $Mn_2(CO)_7[P(OEt)_3]_3$ proceeds very slowly. However, when CO is removed, more extensive substitution occurs, and evidences for radical species are seen. The
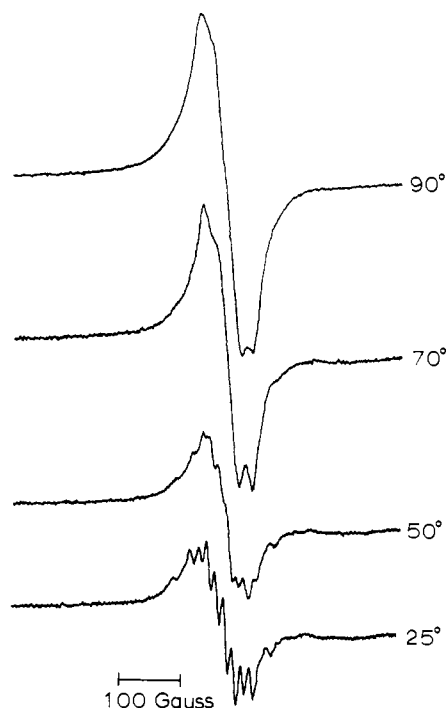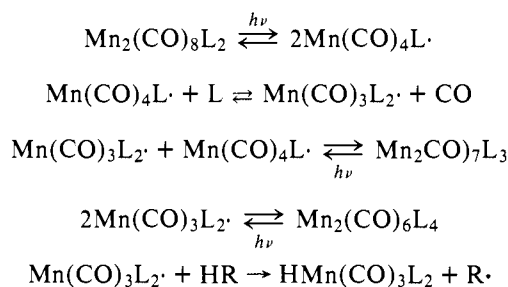
Figure 3. ESR spectrum at various temperatures of heptane solution of $Mn_2(CO)_7[P(OEt)_3]_3$ + $P(OEt_3)_3$ following photolysis.

Figure 4. Frozen solution (83 K) ESR spectrum of $Mn_2(CO)_7[P(OEt)_3]_3$ + $P(OEt)_3$ in heptane, following photolysis.

Scheme I

$$Mn_2(CO)_8L_2 \overset{h\nu}{\rightleftharpoons} 2Mn(CO)_4L\cdot$$

$$Mn(CO)_4L\cdot + L \rightleftharpoons Mn(CO)_3L_2\cdot + CO$$

$$Mn(CO)_3L_2\cdot + Mn(CO)_4L\cdot \underset{h\nu}{\rightleftharpoons} Mn_2CO)_7L_3$$

$$2Mn(CO)_3L_2\cdot \underset{h\nu}{\rightleftharpoons} Mn_2(CO)_6L_4$$

$$Mn(CO)_3L_2\cdot + HR \rightarrow HMn(CO)_3L_2 + R\cdot$$

reactions occurring in the system, as deduced from the results described in the preceding paper, are summarized in Scheme I.

The ESR spectrum obtained upon photolysis of Mn_2-$(CO)_8(PBu_3)_2$ + PBu_3 is satisfactorily simulated by assuming that the paramagnetic species involved is $Mn(CO)_3(PBu_3)_2\cdot$, with idealized square-pyramidal geometry about the metal. The phosphines are assumed to occupy mutually trans basal positions. The spectrum is not perfectly fit, because an axially symmetric g tensor was assumed. In addition, contributions to the line shape due to [55]Mn quadrupolar transitions are neglected, whereas these could be of importance.[35] However, the fit (Figure 2) is quite satisfactory, and leaves little doubt that the radical species is correctly characterized. Ozin has reportedly characterized the $Mn(CO)_5\cdot$ radical isolated in an argon matrix.[36] The Mn hyperfine coupling constants are reported as $A_{\parallel}$ = 65.8 and $A_{\perp}$ = 32.8 G. The agreement with our results for the substituted radical (Table II) is satisfactory. In addition, the parameters extracted from the frozen solution spectrum are consistent with the approximate isotropic values derived from the room temperature spectrum, assuming opposite signs for $A_{\parallel}$ and $A_{\perp}$.

The ESR spectrum of the radical species formed in photolysis of $Mn_2(CO)_7[P(OEt)_3]_3$ is qualitatively similar to that observed in the PBu_3 system. The frozen solution spectrum did not provide sufficient detail to warrant attempts at a complete computer fit. Nevertheless, the results indicate that a disub-
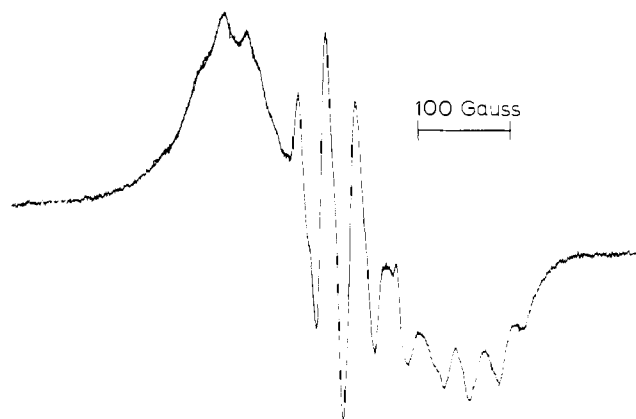
stituted radical, $Mn(CO)_3[P(OEt)_3]_2\cdot$, is formed, and that it has a structure similar to that described above for $Mn(CO)_3$-$(PBu_3)_2\cdot$.

The ESR spectra of $Mn(CO)_3(PBu_3)_2\cdot$ and $Mn(CO)_3$-$[P(OEt)_3]_2\cdot$ support the assumption that the phosphorus ligands are located in basal positions. The IR spectrum of the ESR-active solution that results from photolysis of $Mn_2(CO)_8(PBu_3)_2$ exhibits four bands at 1912, 1861, 1856, and 1836 cm^{-1}. These are sufficient in number to account for the three IR-active CO stretching modes expected for $Mn(CO)_3(PBu_3)_2\cdot$, assuming trans-basal PBu_3 groups. Similarly, Poë and co-workers have observed three IR bands, at 1988, 1912, and 1862 cm^{-1}, for the product of the reaction of $Mn_2(CO)_8(PPh_3)_2$ with PPh_3, which they conclude is $Mn(CO)_3(PPh_3)_2\cdot$. The CO stretching modes assigned to $Mn(CO)_5\cdot$ in the co-condensation of Mn atoms and CO are at 2058 (vw), 1938 (ms), and 1911 cm^{-1} (m).[38]

Because we have not been able as yet to isolate the radical species, the IR spectra are not very useful in deducing the geometry. Perhaps more significant is the observation that in the hydrides formed by abstraction of a hydrogen atom from solvent the mer isomers, i.e., 1-H,2,4-L isomer,[2] is formed. While the evidence is not compelling, this suggests that the phosphorus ligands are in trans-basal positions in the radical.

Recombination of the substituted monomeric species to form the substituted dimers is impeded by the steric requirements of L. Repulsive interactions between L and CO or the L group on the other metal center serve to destabilize dimers with L groups in equatorial positions. In $Mn_2(CO)_9L$ or $Mn_2(CO)_8L_2$ when L is a phosphorus ligand, only for L = PH_3 is the ligand in an equatorial position.

Thus, it appears that formation of dimers substituted with phosphorus ligands, or others of similar bulk, from the radical monomers requires rearrangement of the monomers to a less stable configuration with L axial. This means that there should be a barrier to recombination of substituted monomers to form the dimer; the height of the barrier will depend largely on the energy difference between the isomers of the monomer in which L is in a basal as compared with the axial position, as depicted in Figure 5A.

Not much is known about the ligand characteristics that make for preferential siting in the basal position. There is some indication from comparative rates of CO dissociation from substituted six-coordinate metal carbonyl compounds that in the 16-electron, five-coordinate species $M(CO)_4L$, the preference for occupancy of a basal position is greatest for those ligands which are weakest π acceptors, and for relatively poor σ donors as well.[39] If the same criteria apply for the 17-electron species, then the energy difference between axial and basal isomers of the $Mn(CO)_4L\cdot$ species should be greater for L =
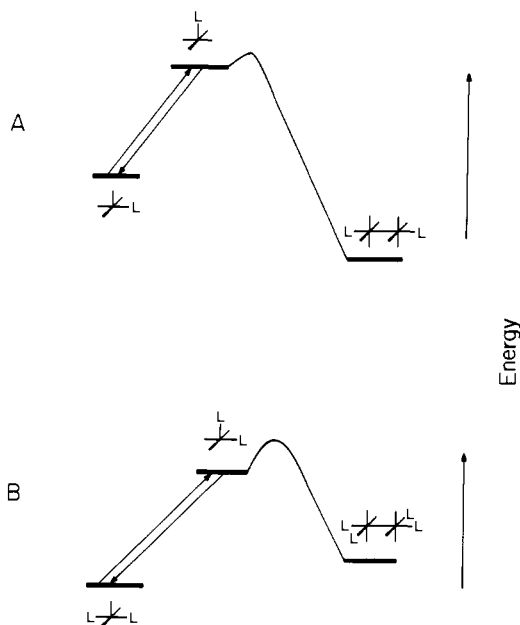
Figure 5. Energetics of formation of substituted metal carbonyl dimers from substituted mononuclear metal carbonyl radicals.

PBu_3 than $L = P(OEt)_3$. It is a corollary of this hypothesis that the substituted dimers, $9,10\text{-}Mn_2(CO)_8L_2$, should be more susceptible than $Mn_2(CO)_{10}$ to metal–metal bond homolysis, to the extent of the destabilizing effects just described. Thus, it is not surprising that thermal metal–metal bond homolysis is more facile in $Mn_2(CO)_8(PPh_3)_2$ than in $Mn_2(CO)_{10}$.[25,40] Similarly, the longer wavelength observed for λ_{max} of the absorption ascribed to the $\sigma-\sigma^*$ transition in the substituted dimers[17,41] could be associated with a weaker metal–metal interaction resulting from the unfavorable ligand siting. The role of ligand steric requirements in weakening the metal–metal bond has been noted also by Jackson and Poë.[42]

When one or both of the monomeric radicals is disubstituted, it is impossible to avoid a sterically unfavorable siting of at least one L in an equatorial position in the dimer. When $L = PBu_3$ dimers of the formula $Mn_2(CO)_{10-n}L_n$, with $L \geqslant 3$, are not observed, indicating that steric interactions prevail over metal–metal bond formation. On the other hand, for the smaller $P(OEt)_3$ (cone angle for $PBu_3 = 132°$, cone angle for $P(OEt)_3 = 109°$),[43] the trisubstituted compound is readily isolable.[17] There is indication in the experimental results that the dimer $Mn_2(CO)_6[P(OEt)_3]_4$ is in equilibrium with a substantial concentration of monomeric radicals:

$$Mn_2(CO)_6[P(OEt)_3]_4 \rightleftharpoons 2Mn(CO)_3[P(OEt)_3)]_2 \quad (1)$$
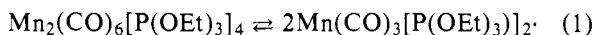
The energetics of the equilibrium may be as suggested in Figure 5B, which shows the free energies of the dimer and monomer species as similar. The barrier to dimer formation involves two major contributions: rearrangement of the monomeric radicals to place one of the phosphite groups in the axial position, and the steric repulsions involving the two equatorial phosphite groups in the course of dimer formation. The ESR results suggest that the barrier to recombination is substantial. However, additional studies are needed to more fully characterize the equilibria involved. Hydrogen atom abstraction by the radicals at higher temperatures must be taken into account.

One of the characteristic reactions of the disubstituted radicals formed in the photolysis experiments is abstraction of hydrogen from solvent to form the corresponding hydride. In a relatively poor hydrogen atom donor solvent such as heptane this is a comparatively slow reaction. On the other

hand, in a solvent such as xylene, hydride is formed much more readily.[11] Under comparable conditions, e.g., in xylene solvent, abstraction occurs more rapidly for the phosphite-substituted species. Also, the qualitative indications are that hydride formation occurs more readily for the more highly substituted radicals. These observations are consistent with the idea that replacement of CO by phosphorus donor ligands strengthens the M–H bond in the cis position.

A second possible mode of reaction for the radical species formed upon substitution is electron transfer. It has been reported that thermal reaction or photolysis of dinuclear metal carbonyl compounds with a variety of ligands results in a disproportionation to yield any of several products, depending on the metal, substituting ligand, and solvent.[44,45] It has been postulated that such photochemical disproportionations result from heterolytic cleavage of the metal–metal bond.[44] We believe that they occur as a result of homolysis, followed by rapid substitution, and subsequently by electron transfer reactions involving the substituted radicals.[46]

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Metal Clusters in Catalysis. 15.[1a] A Structural and Chemical Study of a Dinuclear Metal Complex, $[\eta^3\text{-}C_3H_5Fe(CO)_3]_2$

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Abstract: The crystal and molecular structure of $[\eta^3\text{-}C_3H_5Fe(CO)_3]_2$ crystallized from pentane at -78 °C was solved from x-ray diffraction data collected from a single crystal. The crystals belong to the monoclinic space group $P_{2_1/n}$ with unit cell dimensions $a = 8.356$ (7) Å, $b = 9.400$ (9) Å, $c = 9.315$ (9) Å, $\beta = 91.13$ (2)°, $V = 731.42$ Å³; $\rho_{calcd} = 1.643$ g/cm³ for $Z = 2$. Full-matrix least-squares refinement, including the third cumulant of probability density function of the structure factor equation, yielded an R factor of 0.069 and a weighted R factor of 0.049 for 1675 observed reflections. This dimeric iron complex lies on a crystallographic center of inversion and has a trans arrangement of the trihapto allyl ligands. The iron-iron distance is surprisingly long, 3.138 (3) Å, although this distance is consistent with the low enthalpy value for dimer dissociation in the solution phase. The coordination sphere about an iron atom may be best described as pseudooctahedral with the allyl ligand considered a bidentate ligand. In solution, $[\eta^3\text{-}C_3H_5Fe(CO)_3]_2$ slowly decomposed to give an array of compounds: propene, $Fe(CO)_5$, $Fe_3(CO)_{12}$, and a set of three ferracyclopentadiene molecules. The metallacycles included tricarbonyl[tricarbonyl(2-ethylferracyclopentadiene)]iron (**1**), hexacarbonyl[dicarbonyl(2-ethylferracyclopentadiene)]diiron (**2**), and tricarbonyl[tricarbonyl(2-hydroxyferracyclopentadiene)]iron (**3**). Hydrogenation of $[\eta^3\text{-}C_3H_5Fe(CO)_3]_2$ proceeded rapidly at 25 °C to form propene, with small amounts of propane, and $C_3H_6Fe(CO)_4$ in addition to $Fe_3(CO)_{12}$ and the ferracyclopentadiene **2**. Reaction of the allyliron dimer with butadiene gave $\eta^4\text{-}C_4H_6Fe(CO)_3$.

Introduction

Dinuclear metal complexes may be considered as cluster prototypes and may in their chemistry provide insights to reactions that occur on metal surfaces. The extent of the metal-metal interaction in these dimers varies quite extensively. There are the robust dimers with quadruple[2,3] and triple[2,4] bonds, two classes that have been extensively investigated in a structural context and which exhibit reactivities that might be exploited in a catalytic context. There is a presently smaller class of dimers that appears to have metal-metal double bonds.[5] Finally, there is a large class in which there is nominally a single metal-metal bond. In this last class, the metal-metal bond is often the weakest in the dimeric molecule. One contributing factor to the metal-metal bond fragility is the nonbonding repulsion forces generated by the plethora of ligands typically attached to the metal atoms in this class of dimers. Thus, the chemistry of these dimers often may be dominated by a first step dissociative process that generates two mononuclear complexes that usually are 17-electron species. These then would not be models of metal surfaces in chemical reactions. This class does, however, present the possibility of generating reactive mononuclear fragments that could be intermediates in chain reactions. Brown and co-workers[6] have elegantly demonstrated that 17-electron complexes in some cases display facile ligand dissociation to give very reactive 15-electron species and that such species are often key chain intermediates in radical-initiated substitution reactions of six-coordinate molecules like $HRe(CO)_5$.

We are exploring the solution chemistry of metal-metal bonded organometallic dimers in an effort to delineate the chemistry of the monomers derived from these dimers. Earlier we established the enthalpy of dissociation of $[\eta^3\text{-}C_3H_5Fe(CO)_3]_2$ and several phosphine and phosphite derivatives of this allyliron dimer.[7] The enthalpies are quite low, 13.5 kcal/mol for the parent tricarbonyl. Hence, the solution chemistry of the monomer $\eta^3\text{-}C_3H_5Fe(CO)_3$ is accessible over a wide range of temperatures, -100 to 50 °C (above ~50 °C rapid thermal decomposition ensues). We describe here the structure for the dimer in the solid state and the solution-phase chemistry of the complex.

Results and Discussion

Description of the Structure. A three-dimensional view of the molecular structure is presented in Figure 1, together with the numbering scheme used to define the interatomic distances and angles listed in Tables I and II, respectively. The molecule is centrosymmetric with a crystallographic inversion center located at the midpoint of the iron-iron bond, implying the antirotational configuration.

The most striking feature of the structure is the very long iron-iron bond distance of 3.138 (3) Å. As the covalent radius of iron is estimated from structural data to be near 1.43 Å,[8] the observed bond distance is nearly 0.3 Å greater than anticipated. This is the same situation found in bis(tricarbonyl-η^5-cyclopentadienylchromium),[9] which is structurally very similar to the compound we report. Because of the marked structural