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GENERATION AND CHARACTERIZATION OF $Mn(CO)_3L_2$ ($L_2 = R_2PC_2H_4PR_2$; R = Et, Ph) AND ITS USE IN THE GENERATION OF ORGANIC RADICALS

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Summary

Irradiation of $Mn_2(CO)_{10}$ with the bidentate phosphine 1,2-bis(diethylphosphino)ethane (depe) rapidly yields $[Mn(CO)_3depe]_2$ and $Mn(CO)_3depe$. The two species are in equilibrium in solution, with the dimer present in larger amounts: $[Mn(CO)_3depe]_2 \rightleftarrows 2Mn(CO)_3depe$. The formation of $Mn(CO)_3depe$ proceeds much more readily than the formation of $Mn(CO)_3L_2$ (L = monodentate phosphine complexes). In addition, no side-products are formed as is the case with the monodentate ligands. The ease with which $Mn(CO)_3depe$ can be generated makes it a convenient reagent for the synthesis of organic radicals because the complex abstracts halogen atoms from alkyl and aryl halides: $Mn(CO)_3depe + RX \rightarrow Mn(CO)_3(depe)X + \dot{R}$.

In the course of our research, we have found it necessary on occasion to generate highly endergonic organic radicals at room temperature [1]. One route to organic radicals is the use of organometallic radical complexes to abstract a halogen atom from the appropriate organic halide:

$$\dot{M}L_n + RX \rightarrow ML_nX + \dot{R} \quad (1)$$

Organometallic radicals are conveniently generated by irradiation of a metal–metal-bonded dimer:

$$L_nM\text{–}ML_n \overset{h\nu}{\rightleftarrows} 2\dot{M}L_n \quad (2)$$

Unfortunately, two limitations rendered this approach unsatisfactory for our purposes: (i) the irradiation necessary for the reaction could lead to unwanted photore-

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activity of other components in the system, and (ii) organometallic radicals tend to be unreactive unless X = I or R is a relatively stable (and preferably electronegative) radical, e.g., CCl_3, benzyl [3]. Two factors in particular contribute to the limited reactivity of the ML_n radicals: the lifetime of ML_n is short due to the back-reaction in eq. 2 and the metal center of ML_n tends not to be very electron-rich (and therefore not too prone to oxidation) because the ligands are typically electron-withdrawing Co or Cp groups.

Recently, Brown et al. demonstrated that long-lived radicals of the type $M(CO)_3L_2\cdot$ (M = Mn, Re; L = tertiary phosphine or phosphite) can be generated by irradiation of the corresponding $M_2(CO)_{10}$ dimers in the presence of excess L [4].

$$M_2(CO)_{10} \overset{h\nu}{\rightleftarrows} M(CO)_5 \xrightarrow{L} M(CO)_3L_2 + 2CO \qquad (3)$$

The tendency of these species not to undergo dimerization is assumed to be primarily a result of the great steric bulk of the coordinated phosphine ligands. The generation of $Mn(CO)_3L_2$ via the method requires prolonged irradiation and the frequent removal of the CO generated in order to drive the reaction to completion [4]. We report here the finding that $Mn(CO)_3(L_2)\cdot$ complexes can be conveniently and quantum-efficiently generated by irradiation of 1/2 solutions of $Mn_2(CO)_{10}$ and bidentate phosphines such as 1,2-bis(diethylphoshino)ethane (depe).

Brown also found that the rate at which $M(CO)_nL_{5-n}\cdot$ species abstract halogen from halocarbons is significantly favored by ligands with small cone angles and high electron-donating ability [3b]. In accordance with this, we also report that the complex $Mn(CO)_3$depe$\cdot$ displays a marked tendency to abstract halogen atoms from halocarbons, presumably owing to the electron-richness and small size of the depe ligand. The $Mn(CO)_3$depe complex thus provides a convenient method for the generation of organic radicals from halocarbons. The complex can either be generated in situ for this purpose, or if desired, a solution can be prepared to which the appropriate organic halide can subsequently be added.

Results and discussion

Generation and identification of $Mn(CO)_3$)depe·

Irradiation ($\lambda > 420$ nm) of a degassed benzene solution of $Mn_2(CO)_{10}$ (10 m*M*) and depe (20 m*M*) results in the disappearance of $Mn_2(CO)_{10}$ as observed by infrared (IR) spectroscopy and the appearance in the IR spectrum of a distinctive broad band with a peak at 1886 cm^{-1}. The resulting solution is a vibrant orange-red. In a closed system (such as an IR cell) some degree (ca. 30%) of back-reaction is observed upon leaving the solution in the dark for several minutes.

Addition of CCl_4 (25 m*M*) in the dark to a solution generated as above results in the immediate loss of the orange-red color and the formation of a cloudy yellow mixture containing *fac*-$Mn(CO)_3$(depe)Cl (identified by its CO region IR spectrum (2021s, 1947ms, 1898s cm^{-1}) by comparison with that reported [5] for *fac*-$Mn(CO)_3(PBu_3)_2Br$ (Bu = n-C_4H_9) (2008s, 1938s, 1894s cm^{-1}). Addition in the dark of Bu_3SnH to the solution containing $Mn(CO)_3$depe results in a slow color change from orange-red to yellow. The product of this reaction has bands in the IR spectrum at 1989vs, 1909s, and 1889s cm^{-1}. These bands compare with those reported [6] for $Mn(CO)_3$(dppe)H (dppe = $Ph_2PC_2H_4PPh_2$) at 2003.5, 1933.1, and

1923 cm^{-1}. When the experiment is carried out in benzene-d_6, the ^1H NMR spectrum of the resulting solution has a multiplet at δ 1.9 ppm attributable to coordinated depe, and a 1 : 2 : 1 triplet at δ −9.20 ppm (J(PH) 48.2 Hz). This latter resonance can be compared with that reported by Brown [4b] for $Mn(CO)_3(PBu_3)_2H$ at δ −8.4 ppm. The product of the Bu_3SnH reaction is thus assigned as *fac*-$Mn(CO)_3$(depe)H. The formation of the chloride and hydride products is strongly suggestive of reactions involving the radical complex $Mn(CO)_3$depe · (eqs. 4 and 5).

$$Mn(CO)_3depe\cdot + CCl_4 \rightarrow Mn(CO)_3(depe)Cl + CCl_3^{\cdot} \quad (4)$$

$$Mn(CO)_3depe\cdot + Bu_3SnH \rightarrow Mn(CO)_3(depe)H + Bu_3Sn^{\cdot} \quad (5)$$

By analogy to Brown's work [4] with monodentate phosphines, the $Mn(CO)_3$depe complex is presumably formed by photolysis of the Mn–Mn bond of $Mn_2(CO)_{10}$ followed by substitution of the resulting $Mn(CO)_5$ · with depe:

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2Mn(CO)_5\cdot \quad (6)$$

$$Mn(CO)_5\cdot + depe \rightarrow Mn(CO)_3(depe)\cdot + 2CO \quad (7)$$

Whereas the $Mn(CO)_3L_2$ complexes reported by Brown showed characteristic electronic transition bands in the near UV (600–1500 nm), the orange-red solution showed only an extremely weak absorption with λ_{max} 900 nm. This suggested that the dominant species in solution was not $Mn(CO)_3$depe · but rather the dimer, $[Mn(CO)_3depe]_2$, which is in equilibrium with a small concentration of monomer:

$$[Mn(CO)_3depe]_2 \rightleftarrows 2Mn(CO)_3depe\cdot \quad (8)$$

ESR spectroscopic observations are consistent with the equilibrium proposed in eq. 8. The ESR spectrum of an irradiated solution of $Mn_2(CO)_{10}$ (10 mM) and depe (20 mM) in pentane : benzene (1 : 1) was very nearly the same as that reported for $Mn(CO)_3(PBu_3)_2$ [4]. The intensity of the signal decreased by a factor of five upon cooling from 25 to 0°C with no significant change in the form of the signal being observed. Thus, as would be expected, decreased temperature favors the formation of the diamagnetic dimer. Hereafter we represent the dimer/monomer equilibrium system as $[Mn(CO)_3depe]_n$.

The results above differ most significantly from those reported [4] by Brown involving PBu_3 in two respects: (i) The formation of the disubstituted metal complex proceeds much more readily in the case of the chelating depe ligand. Thus, even in a completely closed system such as an IR cell, the reaction went to ca. 95% completion with 30 s of irradiation. In contrast, with PBu_3 the solution must be subjected to frequent freeze-pump-thaw cycles to remove CO in order to effect the second substitution of the metal center. In no case with depe were $[Mn(CO)_4L]_2$ or other products observed. The former complex is the dominant initial product when $L = PBu_3$. (ii) The equilibrium in eq. 8 greatly favors the dimer whereas when $L = PBu_3$ there is no indication of the formation of any significant amount of the corresponding tetrasubstituted dimer in solution. This can be attributed to the smaller size of the depe ligand when compared with two PBu_3 ligands. The smaller size results in diminished steric repulsion between the two monomers and dimerization can occur. It should also be noted that the phosphine groups of depe are constrained to a *cis* configuration whereas the phosphines of $Mn(CO)_3(PBu_3)_2$ · adopt a *trans* configuration [4].

Reaction with halocarbons

We required a means of generating the radical $CH_2Cl\cdot$ in the presence of $Cp_2Fe_2(CO)_4$ in order to test a hypothesized mechanistic step (eq. 9) in a reaction involving the formation of $CpFe(CO)_2(CH_2Cl)$ from $Cp_2Fe_2(CO)_4$ and CH_2Cl_2 [1].

$$CH_2Cl\cdot + Cp_2Fe_2(CO)_4 \overset{?}{\rightarrow} CpFe(CO)_2(CH_2Cl) + CpFe(CO)_2\cdot \quad (9)$$

In order to duplicate the conditions of the reaction in question, it was necessary to generate the radical at room temperature in the absence of light. In particular, we needed to avoid the possibility of a simple radical recombination reaction between $CH_2Cl\cdot$ and thermally or photolytically generated $CpFe(CO)_2\cdot$.

Addition of a benzene solution of $[Mn(CO)_3depe]_n$ to a benzene solution of CH_2Cl_2 results in the loss of the orange-red color due to the starting complex and the formation of a cloudy yellow solution determined by IR spectroscopy to contain $Mn(CO)_3(depe)Cl$. Presumably, $CH_2Cl\cdot$ is formed concomitantly. When this reaction was carried out in the presence of $Cp_2Fe_2(CO)_4$, neither the disappearance of the iron dimer nor the appearance of $CpFe(CO)_2(CH_2Cl)$ was observed. Consistent with this negative result, subsequent experiments confirmed the viability of an alternative pathway for the formation of $CpFe(CO)_2(CH_2Cl)$ [1].

The addition of $CHBr_3$ to a benzene solution of $[Mn(CO)_3depe]_n$ resulted in an immediate color range from orange-red to pale yellow. The product was $Mn(CO)_3(depe)Br$ as identified by IR spectroscopy: $\nu(C{\equiv}O)$ 2019s, 1948m, and 1897s cm^{-1}. (These values agree closely with those reported for $Mn(CO)_3(PBu_3)_2Br$ [5] and they are nearly identical to those in the spectrum of $Mn(CO)_3(depe)Cl$.) The use of PrBr (Pr = n-C_3H_7) results in a similarly rapid reaction, of which the dominant product is the expected $Mn(CO)_3(depe)Br$. However, another major product is formed with bands at 1984vs, ~ 1905s (shoulder on the 1897 cm^{-1} band of $Mn(CO)_3(depe)Br$), and 1873s cm^{-1}. This spectrum is quite similar to that of $Mn(CO)_3(depe)H$, though red shifted 4–16 cm^{-1}. The most plausible assignment was the complex $Mn(CO)_3(depe)Pr$. This assignment was confirmed by ^1H NMR which revealed a multiplet due to the bridging methylene protons of coordinated depe at δ 2.06 ppm, and a multiplet centered at δ 0.03 ppm attributable to the protons of the α-methylene group. The pattern was nearly a 1 : 4 : 6 : 4 : 1 (J 17.4 Hz) quintuplet which would be expected if $^3J(PH) \approx {}^3J(HH)$. The formation of the alkylmanganese complex is most reasonably explained as the result of a radical combination reaction between $Mn(CO)_3depe\cdot$ and the propyl radical resulting from the bromine abstraction (eqs. 10 and 11). It is not surprising that such a radical combination should be so facile [7,8].

$$Mn(CO)_3depe\cdot + PrBr \rightarrow Mn(CO)_3(depe)Br + Pr\cdot \quad (10)$$

$$Pr\cdot + Mn(CO)_3depe\cdot \rightarrow Mn(CO)_3(depe)Pr \quad (11)$$

In order to reduce the occurrence of reaction 11, the photolytic generation of $Mn(CO)_3depe$ was carried out in the presence of PrBr rather than by adding the halocarbon after irradiation. Since reaction 10 is fast, the steady-state concentration of $Mn(CO)_3depe\cdot$ should remain low under these conditions. The rate of reaction 11 should therefore be greatly decreased as compared with the experiment in which PrBr was added after the irradiation, and the Pr radical formed in reaction 11 should preferentially undergo alternative decomposition reactions, e.g. dimerization,

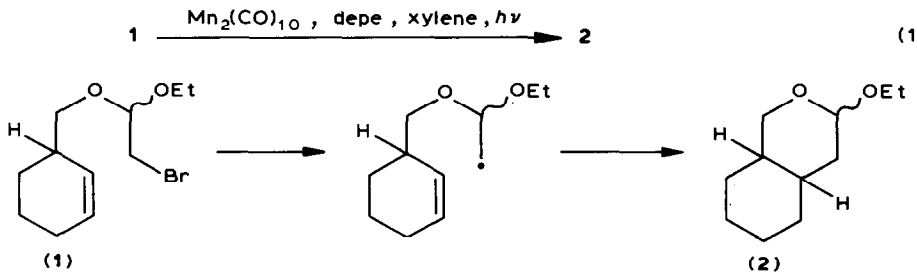
disproportionation, or reaction with solvent and impurities. As expected, irradiation of a solution of $Mn_2(CO)_{10}$ (10 m*M*), depe (25 m*M*), and PrBr (25 m*M*) afforded a better yield of $Mn(CO)_3$(depe)Br than in the original experiment and a greatly decreased amount of $Mn(CO)_3$(depe)Pr as determined by IR spectroscopy. In general it should be noted that unless the reagents involved are photoreactive or reactive towards phosphines, the in situ photolytic generation of the $[Mn(CO)_3depe]_n$ is preferable to generation followed by addition of the halocarbon.

For purposes of comparison, a benzene solution of $Mn_2(CO)_{10}$ (10 m*M*) and PrBr (30 m*M*) containing no depe was irradiated in an IR cell for 2 h. No detectable reaction was observed. An identical solution containing depe (25 m*M*) gave 50% conversion to $Mn(CO)_3$(depe)Br within 15 s of irradiation. On the basis of this result we can conclude that the addition of depe increases the efficiency of the abstraction reaction by a factor of at least 10^4.

When i-PeBr (i-Pe = isopentyl) is added to a solution of $[Mn(CO)_3depe]_n$, bromine atom abstraction proceeds rapidly as evidenced by the change of color and IR spectroscopy. $Mn(CO)_3$(depe)Br is the only product observed; manganese–alkyl bond formation does not occur to any significant extent. Apparently the bulkier i-Pe· radical does not combine with $Mn(CO)_3$depe· as favorably as Pr· (eq. 11).

In order to confirm the formation of organic radicals from the presumed bromine atom abstractions above, reactions were carried out in the presence of the hydrogen-atom donor 1,4-cyclohexadiene (CHD). Irradiation of a benzene solution of $Mn_2(CO)_{10}$ (10 m*M*), depe (25 m*M*), OcBr (25 m*M*) (Oc = n-C_8H_{17}; OcBr was used in place of PrBr to avoid the possible loss of volatile PrH due to degassing) and CHD (1.0 *M*) resulted in the formation of $Mn(CO)_3$(depe)Br (15.2 m*M*) and $Mn(CO)_3$(depe)H (4.8 m*M*). (The atypically high amount of $Mn(CO)_3$(depe)H formed is presumed to be due to the presence of the CHD: $Mn(CO)_3depe + C_6H_8 \rightarrow Mn(CO)_3(depe)H + C_6H_7$). Gas chromatographic analysis of the resulting solution revealed the disappearance of ca. 15 m*M* OcBr and the presence of 14.4 m*M* OcH, a 95% yield based on the amount of $Mn(CO)_3$(depe)Br formed.

The $[Mn(CO)_3depe]_n$ system was also successfully utilized to abstract bromine from the mixed bromoacetal, **1**. Formation of radicals from functionalized organic halides such as **1** is of interest in light of the current renaissance of radical chemistry in organic synthesis [9]. Irradiation of a 1 : 4, xylene : benzene solution of $Mn_2(CO)_{10}$ (10 m*M*), depe (25 m*M*), and **1** (25 m*M*) resulted in rapid bromine transfer as evidenced by the complete disappearance of $Mn_2(CO)_{10}$ and the formation of $Mn(CO)_3$(depe)Br as the only detectable product in the IR spectrum. Thin layer chromatography revealed the clean formation of the diastereomeric mixture of the desired cyclized product (eq. 12), **2**, as determined by comparison with an authentic sample of **2**. The proposed intermediate is also shown below.



The halogen abstraction also proceeded smoothly when the more economical and easily handled dppe was used in place of depe. Note that attempts to prepare $[Mn(CO)_3dppe]_n$ did result in a solution which afforded an ESR signal of the desired radical. However, the IR spectrum revealed a complex mixture of products [10] and upon addition of chlorocarbons, only moderate yields of $Mn(CO)_3(dppe)Cl$ were obtained. Thus the use of the $Mn_2(CO)_{10}$/dppe system should be restricted to applications in which the organic halide is added before irradiation.

In order to determine the selectivity of the $[Mn(CO)_3depe]_n$ system with respect to primary and secondary bromides, a competition experiment was performed. Irradiation of a solution of $Mn_2(CO)_{10}$ (10 m*M*), depe (25 m*M*), CHD (1.0 *M*), OcBr (50 m*M*) and i-PeBr (50 m*M*) resulted in the formation of OcH (4.5 m*M*) and i-PeH (9.5 m*M*) as determined by gas chromatography. Thus, the system exhibits only a moderate preference for the thermodynamically more weakly bonded secondary Br atom.

The formation of aryl radicals is in general considerably more difficult than that of alkyl radicals. Nevertheless, abstraction of bromine from PhBr (Ph = C_6H_5) by $[Mn(CO)_3depe]_n$ proceeds rapidly. After 40 s of irradiation in an IR cell, a solution $Mn_2(CO)_{10}$ (10 m*M*), depe (20 m*M*) and PhBr (0.1 *M*) exhibits an 85% loss of $Mn_2(CO)_{10}$. The CO stretching region of the IR spectrum reveals $Mn(CO)_3(depe)Br$ and a complex of similar symmetry with bands at 1988s, 1895m, and 1868m cm^{-1}, proposed to be $Mn(CO)_3(depe)Ph$. When PhBr (35 m*M*) was added to a benzene-d_6 solution of $[Mn(CO)_3depe]_n$ (20 m*M*) the color change from orange-red to pale yellow occurred over a period of roughly 1 min. (Recall that the reactions with PrBr and i-PeBr occurred immediately upon mixing.) Infrared spectroscopy of the resulting solution revealed the presence of $Mn(CO)_3(depe)Br$ and the compound proposed to be $Mn(CO)_3(depe)Ph$. ^1H NMR showed an unresolved multiplet at $\delta \sim 7.95$ ppm, attributable to the coordinated phenyl group.

Attempts to generate radicals from monochlorocarbons were unsuccessful. No reaction occurred upon the addition of either OcCl or cyclohexyl chloride (40 m*M*) to a solution of $[Mn(CO)_3depe]_n$ (20 m*M*) as monitored by IR spectroscopy. In view of the greater reactivity of $Re(CO)_5\cdot$ than $Mn(CO)_5\cdot$ towards halogen abstraction [3a], we attempted to substitute $Re_2(CO)_{10}$ for $Mn_2(CO)_{10}$ in the metal-dimer/depe system. However, irradiation ($\lambda > 360$ nm) of a benzene solution of $Re_2(CO)_{10}$ (10 m*M*), depe (25 m*M*), and cyclohexyl chloride (40 m*M*) resulted in the formation of metal carbonyl products which were no different than those resulting from an otherwise identical solution which did not contain halocarbon.

Experimental section

$Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, depe, dppe (Strem Chemicals); PrBr, OcBr, i-PeBr, OcCl, cyclohexyl chloride, cyclohexadiene, Bu_3SnH, $CHBr_3$, PhBr, benzene-d_6 (Aldrich); and CCl_4, n-octane, n-pentane, and xylenes (Fischer) were used as received. Benzene was distilled from $LiAlH_4$ and stored under nitrogen.

All solutions were degassed with argon or nitrogen before the addition of depe and irradiation. Irradiations were performed in a septum-covered test tube unless indicated otherwise; a slow flow of inert gas above the solution permitted the escape of any evolved CO.

An Oriel 200 W high-pressure mercury lamp was used for all irradiations. A

Corning CS 3-73 filter ($\lambda > 420$ nm) was used for all irradiations of $Mn_2(CO)_{10}$. A CS 0-52 filter ($\lambda > 360$ nm) was used for the irradiations of $Re_2(CO)_{10}$.

IR spectra were recorded with a Perkin–Elmer 983 spectrometer. ^1H NMR spectra were obtained with a Varian XL-200 FT spectrometer. ESR experiments were performed with a Varian E Line Century Series variable temperature spectrometer. A Cary 17 spectrophotometer was used to obtain UV-visible spectra.

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$$Co(CN)_5^{3-} + RX \rightarrow Co(CN)_5X^{3-} + R\cdot$$

$$Co(CN)_5^{3-} + R\cdot \rightarrow Co(CN)_5R^{3-}$$

Coupling of R· with a metal radical occurs in this case and in reaction 11 because of the relative high concentration of the metal radicals. The metal radical will have a much lower concentration when it is generated by photolysis of a metal–metal-bonded dimer, and the occurrence of reactions analogous to eq. 11 is therefore less likely in these cases.
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