Finally, the resistance of the Co corrin to R· attack as previously noted,[24] the fact that enzyme-free Ado-B_{12} is resistant to the undesirable but established type of side reaction[15,19,25] of Co(II) + $\cdot\mathrm{CH_2}\overline{\mathrm{CHOCH(Ad)CH(OH)C}}\mathrm{H(OH)}$ $\rightarrow$ Co—H + $\mathrm{CH_2{=}}\overline{\mathrm{COCH(Ad)CH(OH)C}}\mathrm{H(OH)}$, and the fact that the enzyme must prevent cyclization of the 5′-deoxyadenosyl radical[26] are additional points worth noting.

Acknowledgment. We wish to thank Dr. C. E. Klopfenstein for his assistance in obtaining high-field NMR spectra. Financial support was provided by NIH Grant AM-26241. R.G.F. is a Dreyfus Teacher-Scholar (1982–1987) and Alfred P. Sloan Foundation Fellow (1982–1984).

Registry No. **1**, 13870-90-1; **3**, 14463-33-3; **4**, 3415-89-2; **5**, 4754-39-6; **6**, 89959-02-4.

Supplementary Material Available: Figures A–E of spectral changes during homolysis, $k_{\mathrm{obsd,Tempo}}$ vs. [Tempo], the slightly curved first-order plots in the absence of Tempo, the $1/k_{\mathrm{obsd}}$ vs. $[\mathrm{B}_{12(\mathrm{r})}]$ plot, and the ln (k_{obsd}/T) vs. $1/T$ plot, respectively, and details on the characterization of the nucleoside products (6 pages). Ordering information is given on any current masthead page.

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Received February 8, 1984

The Most Simple Type of a Manganese Dihalide Phosphine Adduct: $MnI_2(PEt_3)_2$

Sir:

The chemistry of transition-metal phosphine and arsine complexes is well-known and documented[1] with the exception of manganese(II). This must be ascribed to preparative difficulties, which have endured for quite some time. An early report by Naldini[2] on $MnX_2(PPh_3)_2$ has been questioned by McAuliffe et al.,[3] who obtained $MnX_2(OPPh_3)_2$ instead. Bennett et al.[4] fully characterized the first manganese dihalide phosphine adduct $MnCl_2(diphos)_2$. Similar compounds, $MnX_2(dmpe)_2$ (X = Br, I), have subsequently been made by Wilkinson et al.[5] Chelating phosphines seemed to be necessary to obtain stable adducts because, until very recently, compounds of composition $MnX_2(PR_3)$ have been mentioned but not well characterized.[6] Green et al.[7] even stated that they were unable to isolate such compounds. It was highly desirable to know more about this chemistry since some controversy arose about their uptake of dioxygen (and other small molecules).[6–8]

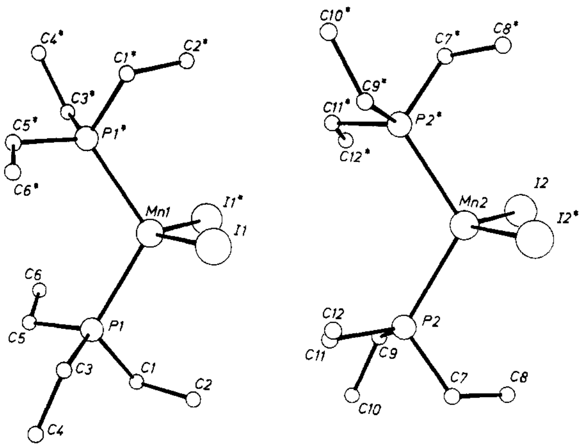

Figure 1.

During our studies on manganocenes and their reaction products such as halides and donor molecule adducts[9] we prepared $MnI_2(PEt_3)_2$, which is expected to simplify the complex situation and which we describe here. When this work was completed, McAuliffe et al.[10] could support their earlier results by a crystal structure of $[MnI_2(PPhMe_2)]_n$.

The title compound is obtained by reaction of anhydrous manganese diiodide[11] in ether with a small excess of triethylphosphine. Recrystallization from ether gives analytically pure[12] pink needles in 47% yield. The X-ray analysis[13] shows two molecuels, **1**/**2** (Figure 1), which are crystallographically different but very similar with respect to their structural pa-

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(12) Anal. Calcd for $C_{12}H_{30}I_2MnP_2$: C, 26.44; H, 5.55; I, 46.57; Mn, 10.07; P, 11.77. Found: C, 25.93; H, 5.47; I, 45.97; Mn, 10.25; P, 11.37.

(13) Crystal data: orthorhombic, *Pccn* (No. 56), $a = 1732.6$ (3) pm, $b = 1730.2$ (3) pm, $c = 1470.2$ (3) pm, $V = 4407.28 \times 10^6$ pm^3, $D_{\mathrm{exptl}} = 1.643$ g cm^{-3} for $Z = 8$, μ(Mo Kα) = 34.80 cm^{-1}, $F(000) = 2104$, $T = 22$ °C. Data collection, structure solution, and refinement: 2897 unique reflections ($\lambda = 71.069$ pm, ω scans, $1 \leq \vartheta \leq 22.5°$, empirical absorption correction, Syntex P2_1), heavy-atom methods, $R = 0.050$, $R_w = 0.050$ ($\omega = K/\sigma^2$) (F_o), $K = 2.64$ in last cycle for 155 parameters and 1866 observed reflections $F > 4\sigma(F)$ (SHELX 76).

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rameters.[14] Each manganese has only four ligands. Two iodines and two phosphines are arranged such that a crystallographic twofold axis passes through the metal bisecting the angles I–Mn–I* and P–Mn–P*. The resulting distorted tetrahedron is the most simple type of a manganese dihalide phosphine adduct structurally characterized so far. All other known adduct structures contain hexacoordinated manganese,[4,5] in one case alternating with tetracoordinated centers.[10] As a consequence of the low coordination number the bond lengths in **1**/**2** are considerably smaller than most of their counterparts in ref 4, 5, and 10.

A solution of **1**/**2** in (deuterated) benzene yields ^{1}H and ^{13}C signals for the ethyl groups of the phosphine. The room-temperature paramagnetic shifts, $\delta_{298}^{\text{para}}$, are −36.8 ($CH_2$), −654.2 ($CH_2$), −5.5 ($CH_3$), and −158.8 ($CH_3$) (negative sign to high frequency). The shifts are very similar to those found for phosphine-stabilized manganese half-sandwich compounds which contain five unpaired electrons.[9b] The electron spin delocalization most probably proceeds through σ bonds with a hyperconjugative contribution to the large α-carbon shift. With small amounts of oxygen, the benzene solution turns dark green while in THF a blue to violet color is seen. The original pink solutions can be regenerated by bubbling argon through them. This supports earlier reports and is indicative for a reversible binding of dioxygen.[8]

Acknowledgment. We thank the Fonds der Chemischen Industrie, Frankfurt, West Germany, for generous support.

Registry No. MnI$_2$(PEt$_3$)$_2$, 91549-44-9.

Supplementary Material Available: Listings of further crystal structure data and atomic coordinates and anisotropic temperature factors (4 pages). Ordering information is given on any current masthead page.

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(14) Bond lengths in picometers and angles in degrees for **1**/**2**: Mn–P = 252.8 (4)/253.9 (4); Mn–I = 266.2 (2)/267.0 (2); I–Mn–I* = 120.1 (1)/119.9 (1); P–Mn–P* = 115.1 (2)/116.4 (2); I–Mn–P = 105.2 (1)/105.5 (1); I–Mn–P* = 105.8 (1)/105.1 (1).

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Received April 4, 1984

"Photoinduced" Complex Formation

Sir:

Luminescence properties of crown ether complexes with divalent europium ions have been studied recently, and the crown ether complexes are known to exhibit a remarkably intense blue emission under UV irradiation.[1-3]

During the course of our studies, we found that Eu(II) complex formation[4] with crown ethers having a bromoalkyl side chain was extraordinarily induced by UV irradiation and that the Eu(II) luminescence intensity in the complex increased significantly.

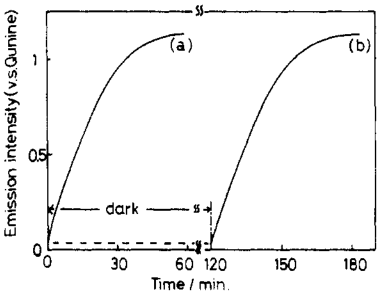

Figure 1. Time dependence of emission intensities for the complex with **1** (excitation 370 nm, emission 440 nm). See text for an explanation of curves a and b.

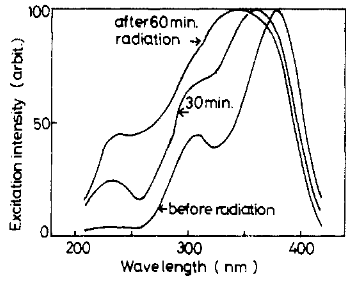

Figure 2. Time dependence of excitation spectra for the complex with **1** (emission 440 nm).

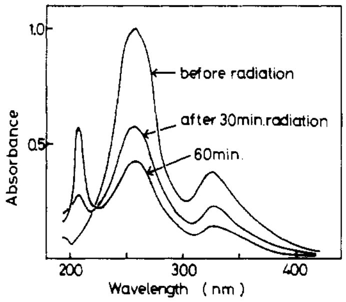

Figure 3. Time dependence of absorption spectra for the complex with **1**. (Concentration of **1**, 8 × 10^{-4} mol dm^{-3}).

The complex of Eu(II) with 2-BrMe-2-Me(15-crown-5) (**1**) gives a strong emission at 423–433 nm with 370-nm excitation. The Eu(II) complex with 2-BrMe-2-Me(18-crown-6) (**2**) shows a 443-nm emission with 376-nm radiation while a simple EuCl$_2$–methanol solution yields an emission peak at 487 nm. These emissions are due to allowed electric dipole transitions between the 5d and 4f states.[6]

The relation between emission intensity vs. irradiation time for an equimolar methanol solution of EuCl$_2$ and **2** is shown in Figure 1. *Curve a* in the figure is for a sample whose emission intensity was measured immediately after the sample preparation and *curve b* for a sample whose emission intensity was taken after keeping the sample in a dark place for 120 min.[7]

As has been reported in previous papers,[1,3] an increase in emission intensity is due to the complex formation of Eu(II)

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(5) The irradiation was done with use of wavelengths of 370 nm for Eu–**1** and 376 nm for Eu–**2** initially, and then these wavelengths were changed according to changes in the excitation maxima for these complexes. The number of photons at the excitation was measured with a Photodyne 66XLA power meter equipped with a No. 350 sensor head and was 4 × 10^{15} photons/s at 370 nm after calibration.

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