

## TRANSITION METAL NITROSYLS AS NITROSYLATION AGENTS

### VI \*. LIGAND REARRANGEMENT BETWEEN THE CARBYLMANGANESE COMPLEXES $[\text{Mn}(\text{CO})_5\text{PR}_3]^+$ AND $[\text{Mn}_2(\text{CO})_{10-n}(\text{PR}_3)_n]$ , AND BIS(HALOGENODINITROSYLCOBALT)

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#### Summary

The UV-induced nitrosylation of neutral and cationic carbonylmanganese compounds by  $[\text{CoX}(\text{NO})_2]_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) is a complex reaction involving the transfer of ligands usually considered as two- ( $\text{CO}$  and  $\text{PR}_3$ ,  $\text{PR}_3 = \text{PEtPh}_2$ ,  $\text{P}(\text{i-Bu})_3$ ,  $\text{P}(\text{O-i-Pr})_3$ ), one- ( $\text{X}$ ), and three-electron donors ( $\text{NO}$ ). The cationic complexes  $[\text{Mn}(\text{CO})_5\text{PR}_3][\text{BF}_4]$  are converted into  $\text{MnBr}_2$ , while  $[\text{Mn}_2(\text{CO})_{10}]$  and its mono- and disubstituted phosphine derivatives readily yield  $[\text{MnL}(\text{NO})_3]$  ( $\text{L} = \text{CO}, \text{THF}, \text{PR}_3$ ), *cis*- $[\text{MnX}(\text{CO})_4\text{PR}_3]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and  $[\text{Co}(\text{CO})_2\text{L}(\text{NO})]$  ( $\text{L} = \text{CO}, \text{PR}_3$ ). Reactivity and product spectrum vary considerably with the starting materials. The only reaction of preparative interest is the conversion of  $[\text{Mn}_2(\text{CO})_{10}]$  to  $[\text{Mn}(\text{THF})(\text{NO})_3]$  by  $[\text{CoCl}(\text{NO})_2]_2$ .  $^{55}\text{Mn}$  and  $^{59}\text{Co}$  NMR characteristics are reported. An optimized preparative route to  $[\text{Mn}_2(\text{CO})_9\text{PEtPh}_2]$  and its  $^{55}\text{Mn}$  NMR spectroscopic feature is also described.

#### Introduction

We have recently shown that dinitrosylcobalt halides are versatile reagents for the high-yield synthesis of nitrosylvanadium compounds such as  $[\text{V}(\text{Cp})\text{CO}(\text{NO})_2]$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5^-$ ) [1],  $[\text{V}(\text{CO})_3\text{diphos}(\text{NO})]$  [2,3],  $[\text{VL}_4(\text{NO})_2]^+$  and  $[\text{VX}(\text{CNR})_3(\text{NO})_2]$  [3,4] from carbonyl complexes by dark (carbonylvanadates) or light-induced reactions. Similarly,  $[\text{Mo}(\text{Cp})(\text{CO})_2\text{NO}]$  can be prepared from  $[\text{Mo}(\text{Cp})(\text{CO})_3]_2$  (light-induced) or  $[\text{Mo}(\text{Cp})(\text{CO})_3]^-$  (at 200 K) and  $[\text{CoX}(\text{NO})_2]_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) in 80% yield [5].

\* For communication V see ref. 4.

We report below our initial results on NO transfer and ligand rearrangement reactions involving carbonylmanganese compounds. In these systems, nitrosylation occurs only under comparatively vigorous conditions, i.e. with UV irradiation.

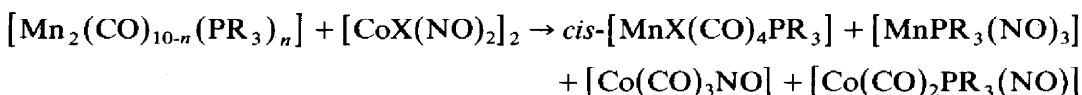
## Results and discussion

*The reaction between  $[\text{Mn}(\text{CO})_5\text{PR}_3][\text{BF}_4]$  ( $\text{PR}_3 = \text{PEtPh}_2, \text{P}(\text{O}-i\text{-Pr})_3$ ) and  $[\text{CoBr}(\text{NO})_2]_2$*

Ultraviolet irradiation of  $[\text{Mn}(\text{CO})_5\text{PEtPh}_2][\text{BF}_4]$  and  $[\text{Mn}(\text{CO})_5\text{P}(\text{O}-i\text{-Pr})_3][\text{BF}_4]$  in THF solution in the presence of  $[\text{CoBr}(\text{NO})_2]_2$  gives  $\text{MnBr}_2$  and Mn (which usually separates as a mirror). The carbonyl and phosphine ligands are partly transferred to cobalt, yielding  $[\text{CoBr}(\text{PR}_3)(\text{NO})_2]$ ,  $[\text{Co}(\text{CO})_2\text{PR}_3(\text{NO})]$  and  $[\text{Co}(\text{CO})_3\text{NO}]$ . This is documented, inter alia, by the  $^{59}\text{Co}$  NMR spectrum of the reaction mixture shown in Fig. 1.  $[\text{Co}(\text{CO})_2\text{PR}_3(\text{NO})]$  can be separated by chromatography on magnesium silicate. For IR and NMR data see Table 1.

*Nitrosylation of  $[\text{Mn}_2(\text{CO})_{10-n}(\text{PR}_3)_n]$  ( $n = 1: \text{PR}_3 = \text{PEtPh}_2; n = 2: \text{PR}_3 = \text{PEtPh}_2, \text{P}(i\text{-Bu})_3, \text{P}(\text{O}-i\text{-Pr})_3$ ) by  $[\text{CoX}(\text{NO})_2]_2$  ( $X = \text{Cl}, \text{Br}, \text{I}$ )*

The overall reaction can be represented by the (non-stoichiometric) equation:



A maximum of 1 mol  $[\text{CoX}(\text{NO})_2]_2$  undergoes reaction per mole of manganese complex. IR and metal NMR data for the various starting materials and reaction products are listed in Table 1. The Table includes  $\delta(^{59}\text{Mn})$  values for  $[\text{Mn}(\text{CO})_4(\mu-$

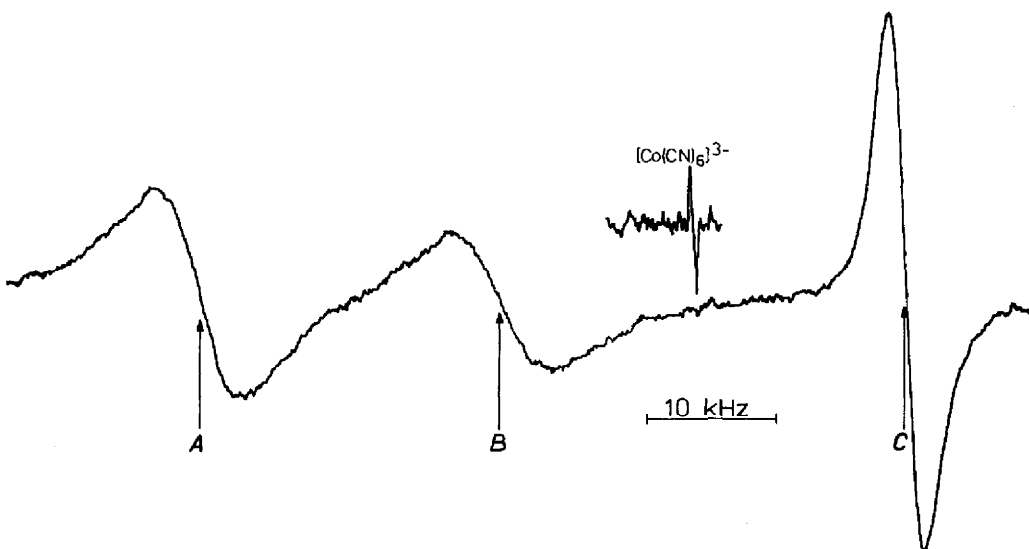


Fig. 1.  $^{59}\text{Co}$  NMR spectrum of the mixture obtained after 3.5 h UV irradiation of  $[\text{Mn}(\text{CO})_5\text{P}(\text{O}-i\text{-Pr})_3][\text{BF}_4]/[\text{CoBr}(\text{NO})_2]_2$  in THF. A:  $[\text{CoBr}(\text{NO})_2]_2$  ( $\delta(^{59}\text{Co}) + 3430$  ppm), B:  $[\text{CoBrP}(\text{O}-i\text{-Pr})_3(\text{NO})_2]$  ( $+ 1360$ ), C:  $[\text{Co}(\text{CO})_2\text{P}(\text{O}-i\text{-Pr})_3(\text{NO})]$  ( $- 1480$ ). The signal for  $[\text{Co}(\text{CO})_3\text{NO}]$  ( $- 1365$ ) is obscured by the broad resonance of C.

Br)]<sub>2</sub> and [Et<sub>4</sub>N][MnBr<sub>2</sub>(CO)<sub>4</sub>] which, according to the <sup>55</sup>Mn spectra observed, are not formed in the ligand rearrangement process.

The tendency to form [MnX(CO)<sub>4</sub>PR<sub>3</sub>] increases in the sequence Cl < Br < I (the formation of this compound is almost completely suppressed if [CoCl(NO)<sub>2</sub>]<sub>2</sub> is the transfer reagent), while the tendency to form [MnPR<sub>3</sub>(NO)<sub>3</sub>] follows the inverse order. The nitrosyl species are also preferentially formed with [Mn<sub>2</sub>(CO)<sub>9</sub>PR<sub>3</sub>] (and [Mn<sub>2</sub>(CO)<sub>10</sub>]; vide infra); this complex also reacts more slowly than [Mn<sub>2</sub>(CO)<sub>8</sub>(PR<sub>3</sub>)<sub>2</sub>]. For the cobalt halides, the reactivity order is Cl > Br > I (cf. Fig. 2). Hence the combination of [Mn<sub>2</sub>(CO)<sub>8</sub>(PR<sub>3</sub>)<sub>2</sub>] and [CoI(NO)<sub>2</sub>]<sub>2</sub> leads to high yields of [MnI(CO)<sub>4</sub>PR<sub>3</sub>], the combination of [Mn<sub>2</sub>(CO)<sub>9</sub>PR<sub>3</sub>] and [CoCl(NO)<sub>2</sub>]<sub>2</sub> to high yields of [MnPR<sub>3</sub>(NO)<sub>3</sub>]. (For discussion of this complex reactivity pattern see the following section.)

The two starting compounds [Mn<sub>2</sub>(CO)<sub>9</sub>PEtPh<sub>2</sub>] and [Mn<sub>2</sub>(CO)<sub>8</sub>(PEtPh<sub>2</sub>)<sub>2</sub>], which are prepared by UV irradiation of [Mn<sub>2</sub>(CO)<sub>10</sub>] plus PEtPh<sub>2</sub> in toluene and

TABLE 1  
IR AND METAL NMR DATA

Complex	$\nu(\text{CO})$ and $\nu(\text{NO})$ <sup>a,b</sup> (cm <sup>-1</sup> )					Phase	$\delta(\text{M})$ <sup>b,c</sup> (ppm)
[Mn <sub>2</sub> (CO) <sub>9</sub> PEtPh <sub>2</sub> ]	2083	2005	1987	(1970)	1929	toluene	-2320/-2420 <sup>d</sup>
[Mn <sub>2</sub> (CO) <sub>8</sub> (PEtPh <sub>2</sub> ) <sub>2</sub> ]	1979	1949				toluene	-2430
[Mn <sub>2</sub> (CO) <sub>8</sub> (P-i-Bu <sub>3</sub> ) <sub>2</sub> ]	1968	1941				toluene	-2430
[Mn <sub>2</sub> (CO) <sub>8</sub> (P(O-i-Pr) <sub>3</sub> ) <sub>2</sub> ]	1987	1955				toluene	-2390
[Mn(CO) <sub>5</sub> PEtPh <sub>2</sub> ][BF <sub>4</sub> ]	2138	2090	2045			CH <sub>2</sub> Cl <sub>2</sub>	-1770
[Mn(CO) <sub>5</sub> P(O-i-Pr) <sub>3</sub> ][BF <sub>4</sub> ]	2140	2080	2050			CH <sub>2</sub> Cl <sub>2</sub>	-1790
[MnCl(CO) <sub>4</sub> PEtPh <sub>2</sub> ]	2082	(2020)	2000	1947		THF	-1080
[MnBr(CO) <sub>4</sub> PEtPh <sub>2</sub> ]	2078	(2015)	1995	1945		THF	-1190 <sup>e</sup>
[MnI(CO) <sub>4</sub> PEtPh <sub>2</sub> ]	2075	(2010)	1995	1950		THF	-1460
[MnBr(CO) <sub>4</sub> P-i-Bu <sub>3</sub> ]	2084	(2020)	1995	1950		THF	<sup>f</sup>
[MnBr(CO) <sub>4</sub> P(O-i-Pr) <sub>3</sub> ]	2075	(2010)	1992	1942		THF	<sup>f</sup>
[Et <sub>4</sub> N][MnBr <sub>2</sub> (CO) <sub>4</sub> ] <sup>g</sup>							+500
[MnBr(CO) <sub>4</sub> ] <sub>2</sub> <sup>g</sup>							-400
[Mn(CO)(NO) <sub>3</sub> ] <sup>h</sup>	1820	1730				THF/pent.	-1170
[Mn(THF)(NO) <sub>3</sub> ] <sup>h</sup>	1773	1670				pentane	-750
[Mn(PEtPh <sub>2</sub> )(NO) <sub>3</sub> ] <sup>i</sup>	1772	(1682)	1675			THF	-1220
[CoCl(NO) <sub>2</sub> ] <sub>2</sub> <sup>j</sup>	1826	1744				THF	+3640
[CoBr(NO) <sub>2</sub> ] <sub>2</sub> <sup>j</sup>	1830	1755				THF	+3390
[CoI(NO) <sub>2</sub> ] <sub>2</sub> <sup>j</sup>	1823	1752				THF	+2790
[Co(CO) <sub>3</sub> NO] <sup>k</sup>	2095	2025	1795			THF	-1365
[Co(CO) <sub>2</sub> PEtPh <sub>2</sub> (NO)] <sup>k,l</sup>	2025	1967	1745			THF	-1430
[Co(CO) <sub>2</sub> P(O-i-Pr) <sub>3</sub> (NO)]	2038	1980	1760			THF	-1480

<sup>a</sup> Wave numbers in parenthesis are shoulders. <sup>b</sup> For [Mn<sub>2</sub>(CO)<sub>10-n</sub>(PR<sub>3</sub>)<sub>n</sub>] see also refs. 7, 8 for [Mn(CO)<sub>5</sub>PR<sub>3</sub>]<sup>+</sup> refs. 7-10. <sup>c</sup>  $\delta(^{55}\text{Mn})$  relative to [MnO<sub>4</sub>]<sup>-</sup>,  $\delta(^{59}\text{Co})$  relative to [Co(CN)<sub>6</sub>]<sup>3-</sup>; all values are given for THF solutions (if not indicated otherwise) and at room temperature. <sup>d</sup> See text for a detailed discussion, and Fig. 3. <sup>e</sup> Width at half-height 3.3 kHz. <sup>f</sup>  $\delta(^{55}\text{Mn})$  are the same as for PR<sub>3</sub> = PEtPh<sub>2</sub> in the limits of error. Compare also [MnBr(CO)<sub>4</sub>PHCy<sub>2</sub>] ( $\delta$  -1130 ppm) [11]. <sup>g</sup> Cf. refs. 28 and 29. <sup>h</sup> NMR data in pentane ([Mn(THF)(NO)<sub>3</sub>]) and THF/pentane ([Mn(CO)(NO)<sub>3</sub>]). Compare also refs. 12 and 13: [Mn(THF)(NO)<sub>3</sub>];  $\nu(\text{NO})$  1178, 1666,  $\delta$  -722. <sup>i</sup> Half-width for the NMR signal = 3.6 kHz.  $\delta$  values for other phosphine derivatives of [Mn(CO)(NO)<sub>3</sub>] are in the range of -1220 ± 30 ppm and correspond with  $\delta$  -1180 ppm reported previously for [MnP(t-Bu)<sub>3</sub>(NO)<sub>3</sub>] [12]. For data see also refs. 13 and 14. <sup>j</sup> From refs. 4 and 6. <sup>k</sup> See also ref. 14. <sup>l</sup> The same data are obtained for [Co(CO)<sub>2</sub>P(i-Bu)<sub>3</sub>(NO)].  $\delta(^{59}\text{Co})$  values differ considerably from that reported for [Co(CO)<sub>2</sub>P(t-Bu)<sub>3</sub>(NO)] (-1116 ppm) [16].

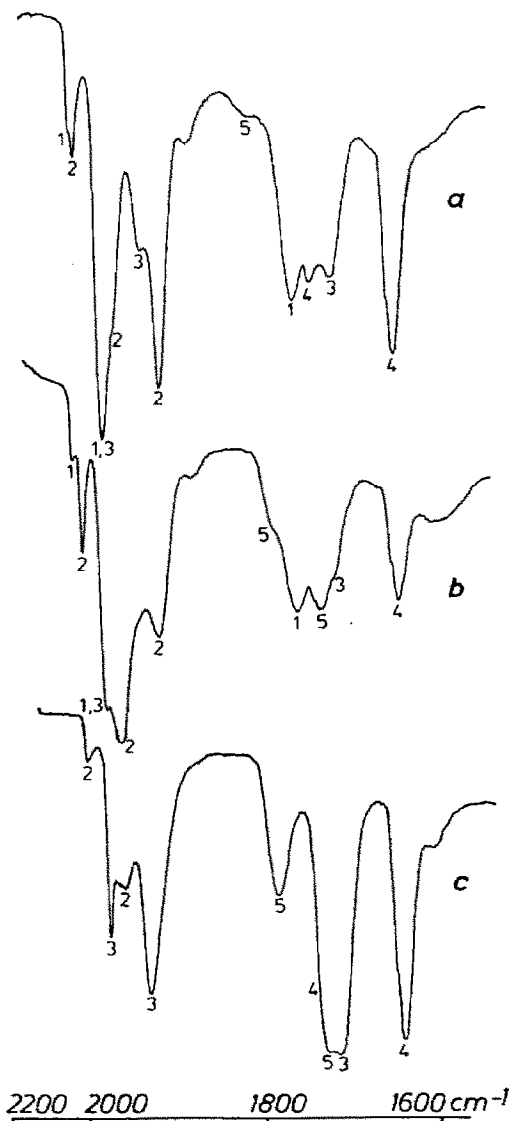


Fig. 2. IR spectra ( $\nu(\text{CO})$  and  $\nu(\text{NO})$  region) for the mixtures obtained from the UV irradiation of  $[\text{Mn}_2(\text{CO})_8(\text{PEtPh}_2)_2]$  and  $[\text{Co}(\text{X})(\text{NO})_2]_2$  (30 min; X = Cl; a, X = I; b), and  $[\text{Mn}_2(\text{CO})_9\text{PEtPh}_2]$  and  $[\text{Co}(\text{I})(\text{NO})_2]_2$  (45 min; c), THF solution. 1:  $[\text{Co}(\text{CO})_3\text{NO}]$ , 2: *cis*- $[\text{MnX}(\text{CO})_4\text{PEtPh}_2]$ , 3:  $[\text{Co}(\text{CO})_2\text{PEtPh}_2(\text{NO})]$ , 4:  $[\text{Mn}(\text{PEtPh}_2)(\text{NO})_3]$ , 5:  $[\text{Co}(\text{X})(\text{NO})_2]_2$ .

separated by column chromatography ( $\text{Al}_2\text{O}_3$ , pentane/ $\text{CH}_2\text{Cl}_2$  10/1) exhibit interesting  $^{55}\text{Mn}$  NMR features: Although the high ( $D_{4d}$ ) symmetry is retained when two CO groups in  $[\text{Mn}_2(\text{CO})_{10}]$  are replaced by  $\text{PEtPh}_2$  [15], the signal of  $[\text{Mn}_2(\text{CO})_8(\text{PEtPh}_2)_2]$  is extremely broad (half-width 22 kHz), in contrast to the sharp signal observed for  $[\text{Mn}_2(\text{CO})_{10}]$  at  $-2277$  ppm [8], and indicating substantial perturbation of the local symmetry at the  $^{55}\text{Mn}$  nucleus (nuclear spin = 5.2, electric nuclear quadrupole moment =  $0.4 \times 10^{-28}$  m<sup>2</sup>) by the bulky and unsymmetrically shaped  $\text{PEtPh}_2$  ligands. The spectrum of  $[\text{Mn}_2(\text{CO})_9\text{PEtPh}_2]$  is a superposition of a broad ( $\{\text{Mn}(\text{CO})_4\text{PEtPh}_2\}$ ) and a narrow signal ( $\{\text{Mn}(\text{CO})_5\}$ , half-width ca. 4 kHz). The spectrum is shown in Fig. 3. The broad component is shifted to lower

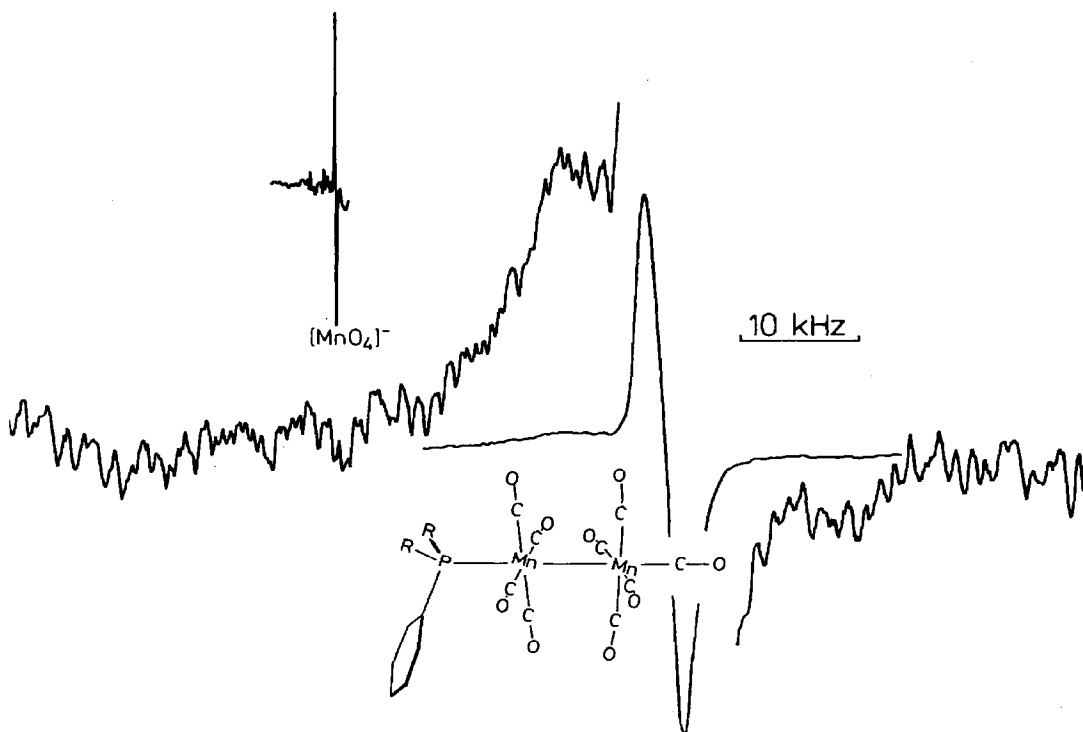


Fig. 3.  $^{55}\text{Mn}$  NMR spectrum (1st. derivative) of  $[\text{Mn}_2(\text{CO})_9\text{PEtPh}_2]$ , showing the two superimposed components for the substituted (broad component at lower field) and the unsubstituted half of the molecule. The structure shown is that for  $[\text{Mn}_2(\text{CO})_9\text{PMe}_2\text{Ph}]$ , adapted from ref. 17.

field by ca. 100 ppm but, as observed previously [8], the overall range for  $\delta(^{55}\text{Mn})$  of  $[\text{Mn}(\text{CO})_{10-n}(\text{PR}_3)_n]$  complexes is small (cf. also Table 1) and cannot be employed to distinguish between different degrees of substitution or variations in the nature of the phosphine ligands.

The work-up of the reaction mixture obtained from the nitrosylation procedure involves several steps:  $[\text{Co}(\text{CO})_3\text{NO}]$  is removed with the solvent THF by evaporation, then the residue is chromatographed on magnesium silicate (pentane/THF) to yield yellow  $[\text{Co}(\text{CO})_2\text{PR}_3(\text{NO})]$  and a green fraction containing the two manganese complexes. Further chromatography of the latter with pentane/toluene leads to isolation of green  $[\text{MnPR}_3(\text{NO})_3]$  and yellow-orange *cis*- $[\text{MnX}(\text{CO})_4\text{PR}_3]$ .

Again, there is no significant change of the metal shieldings in  $[\text{Co}(\text{CO})_2\text{PR}_3(\text{NO})]$  and  $[\text{MnPR}_3(\text{NO})_3]$  on variation of the phosphine ligands (Table 1), which is in contrast with findings for, e.g.,  $\delta(^{51}\text{V})$  in  $[\text{V}(\text{Cp})\text{PR}_3(\text{NO})_2]$  [1,18],  $\delta(^{59}\text{Co})$  in  $[\text{CoX}(\text{PR}_3)(\text{NO})_2]$  [6] and  $\delta(^{59}\text{Co})$  in  $[\text{Co}(\text{CO})_2\text{P}(\text{EMe}_3)_3(\text{NO})]$  [16,19], but agrees with what has been observed for  $\delta(^{55}\text{Mn})$  in the series  $[\text{MnP}(\text{EMe}_3)_3(\text{NO})_3]$  [12] (E = C, Si, Ge, Sn). Further, there is no significant difference between the parent carbonyl compound and its phosphine derivative. On the other hand, change in the halide ligand can cause substantial alterations in  $\delta(^{55}\text{Mn})$ , and the usual normal halogen dependence [20,21] (manganese shielding in  $[\text{MnX}(\text{CO})_4\text{PR}_3]$  increases in the order  $\text{Cl} < \text{Br} < \text{I}$ ) is observed, in keeping with the sequences for  $[\text{MnX}(\text{CO})_5]$  [22] and  $[(\text{CO})_3\text{XMnSN}(\text{Me})\text{PPh}_2]$  [23]. In this context, a consistent decrease of

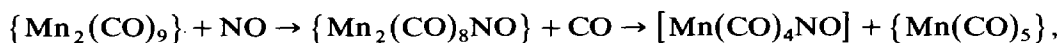
manganese shielding in the series  $[\text{Mn}(\text{CO})_6]^+$  (−1445) [8],  $[\text{MnBr}(\text{CO})_5]$  (−1160) [22],  $[\text{Mn}(\text{CO})_4(\mu\text{-Br})_2]$  (−400) and  $[\text{MnBr}_2(\text{CO})_4]^-$  (+520 ppm) is also of interest.

#### *The nitrosylation of $[\text{Mn}_2(\text{CO})_{10}]$*

As with  $[\text{Mn}_2(\text{CO})_9(\text{PEtPh}_2)]$ , the reaction between  $[\text{Mn}_2(\text{CO})_{10}]$  and  $[\text{CoX}(\text{NO})_2]_2$  needs more intense irradiation (quartz vessel) and longer irradiation times than in the case of  $[\text{Mn}_2(\text{CO})_8(\text{PR}_3)_2]$ . The tendency to preferential formation of the trinitrosyl manganese complex is even more pronounced; practically no  $[\text{MnX}(\text{CO})_5]$  is formed with  $[\text{Mn}_2(\text{CO})_{10}]$ . Only for  $\text{X} = \text{Cl}$  is the reaction complete and, in addition to  $[\text{Co}(\text{CO})_3\text{NO}]$ ,  $[\text{Mn}(\text{THF})(\text{NO})_3]$  (if THF is the solvent) or  $[\text{Mn}(\text{CO})(\text{NO})_3]$  (in pentane/ethanol 10/1), or mixtures of the two trinitrosyl species (in pentane/THF 9/1) are obtained in optimum yields. The THF complex, which is fairly stable below 0°C, can be isolated by evaporation (removal of solvent THF and  $[\text{Co}(\text{CO})_3\text{NO}]$ ) at 0°C, and this reaction may therefore be regarded as an alternative route to the photo-nitrosylation of  $[\text{Mn}_2(\text{CO})_{10}]$  by NO in THF [13]. In contrast to this direct nitrosylation with NO, the intermediate  $[\text{Mn}(\text{CO})_4\text{NO}]$  has not been detected with certainty, using  $[\text{CoCl}(\text{NO})_2]_2$  as the NO transfer agent. As noted previously [12], the  $^{55}\text{Mn}$  nucleus in the THF complex ( $\delta(^{55}\text{Mn}) - 750$  ppm) is deshielded with respect to  $[\text{Mn}(\text{CO})(\text{NO})_3]$  (−1170) and  $[\text{MnPR}_3(\text{NO})_3]$  (−1220 ppm for  $\text{PR}_3 = \text{PEtPh}_2$ ), a fact which is accounted for by the hardness and negligible  $\pi$  acceptor ability of oxygen ligands [3,4,21,24].

#### **Conclusion**

It has been shown that photolysis of  $[\text{Mn}_2(\text{CO})_{10}]$ , both in solution [26] and in the gas phase [27], yields square-pyramidal  $\{\text{Mn}(\text{CO})_5\}$  and (CO-bridged)  $\{\text{Mn}_2(\text{CO})_9\}$  as the initial photo-products, i.e. a seventeen- and a sixteen-electron species which, in a primary nitrosylation step, can react according to



the intermediates being subject to rapid secondary reactions.

Analogous photo-products are expected for  $[\text{Mn}_2(\text{CO})_9\text{PR}_3]$  and  $[\text{Mn}_2(\text{CO})_8(\text{PR}_3)_2]$ , possibly with a preference for the homolytic fission of the Mn–Mn bond over photo-dissociation of carbon monoxide, because the Mn–CO bond is strengthened as  $\text{Mn}(3d_\pi) \rightarrow \text{CO}(\pi^*)$  interaction increases on the introduction of phosphine ligands. The halogen (originally attached to the dinitrosylcobalt moiety), which competes with NO in the ligand transfer reactions, may act as a two-electron ( $\text{X}^-$ ) or a one-electron donor ( $\text{X}\cdot$ ) and can therefore be captured by  $\{\text{Mn}_2(\text{CO})_8\text{L}\}$  ( $\text{L} = \text{CO}, \text{PR}_3$ ) to form  $[\text{Mn}_2(\text{CO})_8\text{L}(\text{X})]^-$ , or by  $\{\text{Mn}(\text{CO})_4\text{L}\}$  to form  $[\text{MnX}(\text{CO})_4\text{L}]$ . The varying tendency for the formation of this latter species, which is observed with the phosphine-substituted dimanganese carbonyls only, and which is observed with an increasing percentage as the one-electron character of the halogen is increasingly emphasized ( $\text{Cl} < \text{Br} < \text{I}$ ), nicely explains the varying reaction pattern in the system  $[\text{Mn}_2(\text{CO})_{10-n}(\text{PR}_3)_n]/[\text{CoX}(\text{NO})_2]_2$ , and supports the assumption of a homolytic scission of the metal–metal bond, followed by two parallel

reaction paths (capture of NO and X, respectively), as the initiating steps at least in the case of  $[\text{Mn}_2(\text{CO})_8(\text{PR}_3)_2]$ .

## Experimental

### General

All operations were carried out under nitrogen and in anhydrous oxygen-free solvents. Three sets of irradiation apparatus (I, II and III) were employed: I and II consisted of a reaction vessel of ca. 400 (I) and 120 ml capacity (II), fitted with a water-cooled quartz immersion well and an externally driven Teflon pump (I) or a filter plate at the bottom (II) to allow agitation of the solution during irradiation by circulation via an external by-pass (I) or by passage of a  $\text{N}_2$  stream through the reaction medium (II). III was a Duran Schlenk tube of ca. 50 ml capacity, fitted with a gas inlet containing a porous disc and closed by a 10 mm mercury valve. UV source was a high pressure mercury lamp (Philips HPK 125) which, in the case of III, was jacketed with a water-cooled Solidex immersion well and placed in the immediate proximity of the Duran vessel.

Carriers for chromatography (neutral aluminum oxide S, 70–290 mesh ASTM, Riedel de Haen; Florisil (magnesium silicate) 200–250 mesh, Merck) were evacuated for 3 h (1 Torr, room temp.) and loaded with  $\text{N}_2$  before use.

### Starting materials

These were prepared by published procedures:  $[\text{CoCl}(\text{NO})_2]_2$  and  $[\text{CoBr}(\text{NO})_2]_2$  [4];  $[\text{CoI}(\text{NO})_2]_2$  [27];  $[\text{Mn}(\text{CO})_5\text{PEtPh}_2][\text{BF}_4]$  [7,10];  $[\text{Mn}_2(\text{CO})_8(\text{P-i-Bu}_3)_2]$  and  $[\text{Mn}_2(\text{CO})_8\{\text{P}(\text{O-i-Pr})_3\}_2]$  [7,8];  $[\text{Et}_4\text{N}][\text{MnBr}_2(\text{CO})_4]$  [28];  $[\text{MnBr}(\text{CO})_4]_2$  [29].

### $[\text{Mn}_2(\text{CO})_9\text{PEtPh}_2]$ and $[\text{Mn}_2(\text{CO})_8(\text{PEtPh}_2)_2]$

The corresponding complexes with  $\text{PMePh}_2$  have been described previously [7], but the lack of experimental details prevented unambiguous reproduction of the separation procedure.

1.01 g (2.58 mmol)  $[\text{Mn}_2(\text{CO})_{10}]$  and 0.55 g (2.57 mmol)  $\text{PEtPh}_2$  were dissolved in 50 ml toluene and irradiated for 1 h (app. II) this being the time needed for an optimum yield of  $[\text{Mn}_2(\text{CO})_9\text{PEtPh}_2]$  (as indicated by IR). The toluene was evaporated (ca. 1 Torr, room temp.), the residue dissolved in 5 ml  $\text{CH}_2\text{Cl}_2$  and treated with 2 ml  $\text{Al}_2\text{O}_3$  carrier. After evaporation of the  $\text{CH}_2\text{Cl}_2$ , the residual powder was transferred to a column ( $50 \times 2$  cm) containing  $\text{Al}_2\text{O}_3$  suspended in n-pentane. Elution with pentane/ $\text{CH}_2\text{Cl}_2$  mixtures successively yielded unreacted  $[\text{Mn}_2(\text{CO})_{10}]$  (20/1, 6 h),  $[\text{Mn}_2(\text{CO})_9\text{PEtPh}_2]$  (10/1, 5 h), and  $[\text{Mn}_2(\text{CO})_8(\text{PEtPh}_2)_2]$  (1/1, 1 h). The fractions containing the phosphine-substituted products were evaporated and dried under high vacuum for 4 h to yield orange coloured, pure powders of  $[\text{Mn}_2(\text{CO})_9\text{PEtPh}_2]$  (0.48 g, 32%) and  $[\text{Mn}_2(\text{CO})_8(\text{PEtPh}_2)_2]$  (0.75 g, 38%).

### $[\text{Mn}(\text{CO})_5\text{P}(\text{O-i-Pr})_3][\text{BF}_4]$

The procedure described here is an optimized version of those used previously for various cationic carbonyl phosphine manganese complexes [7–10].

A  $\text{CH}_2\text{Cl}_2$  solution containing 8.51 g (11.3 mmol)  $[\text{Mn}_2(\text{CO})_8\{\text{P}(\text{O-i-Pr})_3\}_2]$ , prepared by UV irradiation (app. I) of  $[\text{Mn}_2(\text{CO})_{10}]/\text{P}(\text{O-i-Pr})_3$  1/2 in toluene, was

treated portionwise with excess  $\text{NO}[\text{BF}_4]$  until  $\text{NO}$  evolution ceased. The initially orange coloured solution turned dark brown and was stirred until it became light again (ca. 1 h). Filtration and removal of the solvent in vacuo yielded a reddish oil, consisting of  $[\text{Mn}(\text{CO})_5\text{P}(\text{O}-i\text{-Pr})_3][\text{BF}_4]$  and small amounts of *cis*- $[\text{Mn}(\text{CO})_4\{\text{P}(\text{O}-i\text{-Pr})_3\}_2][\text{BF}_4]$  (by IR). The oil was treated with 10 ml portions of *n*-hexane, until the supernatant solution remained colourless. After decantation, the residue was dissolved in THF, treated with hexane until the solution became slightly turbid, and set aside at  $-18^\circ\text{C}$  for 24 h. Filtration of the white, micro-crystalline product and high vacuum drying gave 2.06 g (38%) pure  $[\text{Mn}(\text{CO})_5\text{P}(\text{O}-i\text{-Pr})_3][\text{BF}_4]$ .

### Spectra

IR spectra were recorded on a Perkin-Elmer 577 spectrometer as 0.01 to 0.02 *M* solutions in 0.1 mm KBr cells.  $^{55}\text{Mn}$  and  $^{59}\text{Co}$  NMR spectra were scanned as the first derivative of the absorption signals on a Bruker SWL 3-100 wideline spectrometer as ca. 0.05 *M* solutions (14 mm diameter vials) at 16 MHz and a central field of 1.520 ( $^{55}\text{Mn}$ ) and 1.585 ( $^{59}\text{Co}$ ) T, respectively. External standards were saturated aqueous  $\text{K}[\text{MnO}_4]$  and  $\text{K}_3[\text{Co}(\text{CN})_6]$ , common sweep widths 5 mT, modulation amplitudes 0.05 to 1 mT, number of scans 10 to 100 (5 min, time constant 1 s). Depending on the line widths, the absolute error is  $\pm 10$  to  $\pm 30$  ppm.

### Reactions

$[\text{Mn}(\text{CO})_5\text{PR}_3][\text{BF}_4]$  and  $[\text{CoBr}(\text{NO})_2]_2$ . Preparation of  $[\text{Co}(\text{CO})_2\text{PEtPh}_2(\text{NO})]$ : 1.1 g (2.2 mmol)  $[\text{Mn}(\text{CO})_5\text{PEtPh}_2][\text{BF}_4]$  and 822 mg (2.2 mmol)  $[\text{CoBr}(\text{NO})_2]_2$ , dissolved in 110 ml THF, were irradiated (app. II) for 155 min. (After this time, IR and NMR absorptions characteristic of the cationic carbonyl-manganese complex had disappeared.) The solution, containing unreacted dinitrosylcobalt bromide,  $[\text{Co}(\text{Br})\text{PEtPh}_2(\text{NO})_2]$ ,  $[\text{Co}(\text{CO})_3\text{NO}]$  and  $[\text{Co}(\text{CO})_2\text{PEtPh}_2(\text{NO})]$ , was freed from insoluble products (mainly  $\text{MnBr}_2$ ) by filtration and evaporated to dryness (removal of  $[\text{Co}(\text{CO})_3\text{NO}]$ ), then the residue was stirred with 30 ml *n*-pentane. After filtration, the pentane solution (now enriched in  $[\text{Co}(\text{CO})_2\text{PEtPh}_2(\text{NO})]$ ) was concentrated to 5 ml and chromatographed on Florisil (35  $\times$  3 cm) with *n*-pentane/THF 10/1 to yield a yellow fraction of pure  $[\text{Co}(\text{CO})_2\text{PEtPh}_2(\text{NO})]$ . The reaction with  $[\text{Mn}(\text{CO})_5\text{P}(\text{O}-i\text{-Pr})_3][\text{BF}_4]$  was carried out similarly.

$[\text{Mn}_2(\text{CO})_{10-n}(\text{PR}_3)_n]$  and  $[\text{CoX}(\text{NO})_2]_2$ . Preparation of  $[\text{MnPEtPh}_2(\text{NO})_3]$ , *cis*- $[\text{MnBr}(\text{CO})_4\text{PEtPh}_2]$  and  $[\text{Co}(\text{CO})_2\text{PEtPh}_2(\text{NO})]$ . The following reactions were carried out:  $n = 1$ ;  $\text{PR}_3 = \text{PEtPh}_2$ ;  $\text{X} = \text{I}$  (app. II),  $n = 2$ ;  $\text{PR}_3 = \text{PEtPh}_2$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$  (app. III),  $n = 2$ ;  $\text{PR}_3 = \text{P}(\text{O}-i\text{-Pr})_3, \text{P}(i\text{-Bu})_3$ ;  $\text{X} = \text{Br}$  (app. III).

The general procedure is described for  $n = 2$ ,  $\text{PR}_3 = \text{PEtPh}_2$  and  $\text{X} = \text{Br}$ : 910 mg (1.19 mmol)  $[\text{Mn}_2(\text{CO})_8(\text{PEtPh}_2)_2]$  and 475 mg (1.20 mmol)  $[\text{CoBr}(\text{NO})_2]_2$  were dissolved in 25 ml THF and irradiated. IR monitoring showed the reaction to be complete after 50 min. Small amounts of insoluble product were filtered off and the solvent and the orange  $[\text{Co}(\text{CO})_3\text{NO}]$  were removed by vacuum distillation (ca. 5 Torr, room temp.). The remaining brown residue, containing  $[\text{Mn}(\text{PEtPh}_2)(\text{NO})_3]$ , *cis*- $[\text{MnBr}(\text{CO})_4\text{PEtPh}_2]$ ,  $[\text{Co}(\text{CO})_2\text{PEtPh}_2(\text{NO})]$ , and a little unreacted  $[\text{CoBr}(\text{NO})_2]_2$ , was dissolved in 30 ml *n*-pentane, and the solution was filtered, concentrated to 5 ml, and transferred to a Florisil column (30  $\times$  3 cm). Yellow  $[\text{Co}(\text{CO})_2\text{PEtPh}_2(\text{NO})]$  was eluted with *n*-pentane/THF 20/1, then elution with



pentane/THF 7/1 gave a green fraction containing the two manganese complexes. This fraction was evaporated to dryness and redissolved in 1 ml toluene, and the solution was transferred to a column (15 × 2 cm) of Florisil suspended in pentane. Chromatography with pentane/toluene 5/1 gave a green solution of  $[\text{MnPEtPh}_2(\text{NO})_3]$ , and, after removal of the solvent, a green, viscous oil of the product. *cis*- $[\text{MnBr}(\text{CO})_4\text{PEtPh}_2]$  was finally extracted with THF and isolated as a yellow-orange powder.

$[\text{Mn}_2(\text{CO})_{10}]$  and  $[\text{CoX}(\text{NO})_2]_2$  ( $X = \text{Cl}, \text{Br}$ ). Preparation of  $[\text{Mn}(\text{THF})(\text{NO})_3]$  and  $[\text{MnCO}(\text{NO})_3]$ : A solution of  $[\text{Mn}_2(\text{CO})_{10}]$  (1.18 g, 3 mmol) and  $[\text{CoCl}(\text{NO})_2]_2$  (0.926 g, 3 mmol) in 120 ml of THF was irradiated (app. II) for 1.5 h, while the solution was agitated vigorously with a strong  $\text{N}_2$  stream. After this time, the only products present in solution were  $[\text{Mn}(\text{THF})(\text{NO})_3]$  and  $[\text{Co}(\text{CO})_3\text{NO}]$ . The solution was filtered, and  $[\text{Co}(\text{CO})_3\text{NO}]$  was slowly removed together with the solvent by evaporation (ca. 1 Torr) at 0°C, leaving green, oily, spectroscopically pure  $[\text{Mn}(\text{THF})(\text{NO})_3]$ . Yield: 410 mg = 31% with respect to  $[\text{Mn}_2(\text{CO})_{10}]$  and 47% with respect to  $[\text{CoCl}(\text{NO})_2]_2$ .

The same procedure with  $[\text{CoBr}(\text{NO})_2]_2$  left ca. 10% of the starting materials unreacted.

A ca. 1/1 mixture of  $[\text{Mn}(\text{THF})(\text{NO})_3]$  and  $[\text{Mn}(\text{CO})(\text{NO})_3]$  was obtained from the reaction between  $[\text{Mn}_2(\text{CO})_{10}]$  and  $[\text{CoCl}(\text{NO})_2]_2$  in pentane/THF 9/1. In pentane/EtOH 10/1,  $[\text{Mn}(\text{CO})(\text{NO})_3]$  was formed together with  $[\text{Co}(\text{CO})_3\text{NO}]$ .

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