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Synthesis of new neutral and cationic monocarbonyl complexes of manganese with bipyridine ligands

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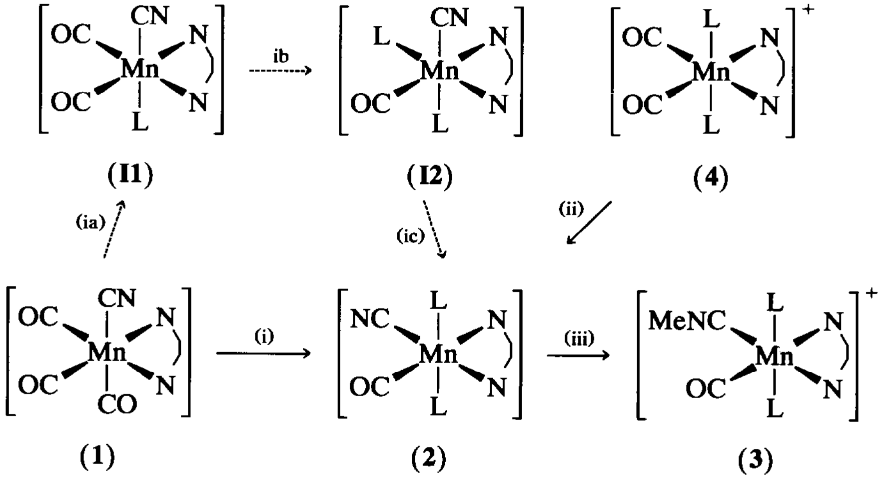
Abstract

The irradiation with UV light at −12°C of the neutral complexes *fac*-[Mn(CN)(CO)$_3$(NN)] (NN = bipyridine, or 4,4′-dimethylbipyridine) in the presence of L = P(OR)$_3$ (R = Me, Et or Ph) in CH_2Cl_2 gave the neutral monocarbonyls of formula *trans*-[Mn(CN)(CO)(NN)L$_2$]. These complexes reacted with MeI and KPF_6 in THF at room temperature to give the new cationic methyl-isocyanide monocarbonyls *trans*-[Mn(CNMe)(CO)(NN)L$_2$]PF_6.

1. Introduction

Many octahedral manganese monocarbonyls have been prepared by photochemically induced CO-substitution from a tri- or di-carbonyl derivative employing PF_3, P(OR)$_3$, diphosphines, polyphosphines or isocyanides as entering ligands [1–5]. Under UV irradiation the cationic complexes *fac*-[Mn(CO)$_3$(NN)L]ClO_4 (NN = bipy or phen) react with L = P(OR)$_3$ or P(OR)$_2$R in CH_2Cl_2 to give *mer*-[Mn(CO)(NN)L$_3$]ClO_4 [6]. In contrast, some cationic manganese monocarbonyl complexes with one CNMe ligand can be prepared starting from a neutral CN precursor and MeI [7,8]. Here we describe the photochemical reaction of the neutral cyanide complexes *fac*-[Mn(CN)(CO)$_3$(NN)] (NN = bipyridine or 4,4′-dimethylbipyridine) with alkyl or aryl phosphites (L), and the two-step synthesis of the new cationic manganese isocyanide-monocarbonyls *trans*-[Mn(CNMe)(CO)(NN)L$_2$]PF_6.



Scheme. 1. (i) L in CH_2Cl_2, $h\nu$ at −12°C; (ii) (PPN)CN in CH_2Cl_2, $h\nu$ at −12°C; (iii) MeI + KPF_6 in THF at room temperature.

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2. Results and discussion

The complexes *fac*-$[Mn(CN)(CO)_3(NN)]$ (**1**) (NN = bipyridine (**1a**) or 4,4′-dimethylbipyridine (**1b**)) react with the phosphites L = $P(OR)_3$ (R = Me, Et, or Ph) in CH_2Cl_2 under UV irradiation at −12°C (reaction (i) in Scheme 1) to give the neutral cyanide carbonyls *trans*-$[Mn(CN)(CO)(NN)L_2]$ (**2a–2f**). During the reaction, some decomposition occurs, with formation of unidentified materials that are paramagnetic. Thus, we noted that the crude reaction products had magnetic susceptibilities that varied from one sample to another, and only after having been washed with water and recrystallized were the samples diamagnetic *. The cyanomonocarbonyls **2** are green-black crystalline solids, except for L = $P(OPh)_3$, which are violet. However, in solution, the colours are different and depend on the solvent and the concentration. This effect is more pronounced in the case of the violet $P(OPh)_3$ derivatives, which are given in less concentrated solutions. The complexes tend to decompose slowly in solution liberating $P(OR)_3$.

The analytical data (Table 1), conductivities, and spectroscopic properties of the isolated cyanocarbonyls **2** were in accord with the structure proposed in Scheme 1. Thus, the values of the molar conductivities in 5×10^{-4} M acetone solution (of the order of 5–10 Ω^{-1} cm^2 mol^{-1}) indicate that these complexes are neutral, and the presence of the CN ligand and only one CO ligand are clearly shown by a medium intensity ν(CN) band at about 2050–2070 cm^{-1}, and an intense and broad single ν(CO) absorption at about 1840–1870 cm^{-1}, in the IR spectrum ** (Table 1). The ^{31}P, ^{1}H and ^{13}C NMR spectra of the complexes $[Mn(CN)(CO)(NN)L_2]$ (Tables 1 and 2) at room temperature showed not only the expected signals from the NN and L ligands, but clearly indicated that the two phosphite

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* Thus, in the case of the complex with bipyridine and $P(OEt)_3$, the crude unwashed product was dissolved in CH_2Cl_2 and partially precipitated with hexane at −20°C, giving a brown solid with specific magnetic susceptibility at 20°C of 24×10^{-6} cgs units, and a green solution that was dried to give a green solid with a susceptibility of 10.9×10^{-6} cgs units. The samples of the compound $[Mn(CN)(CO)(Me_2\text{-bipy})\{P(OPh)_3\}_2]$ had specific susceptibilities at 20°C that ranged from 3.8×10^{-6} to 6.9×10^{-6} cgs units, depending on the purification, and a sample of crude $[Mn(CN)(CO)(bipy)\{P(OPh)_3\}_2]$ had a magnetic susceptibility of 9.8×10^{-6} cgs units, but after having been washed with water, dried, and recrystallized it was diamagnetic.

** The crude products of the reactions that had not been washed with water, had higher ν(CO) and lower ν(CN) frequencies (the latter being more intense). This effect was more pronounced in the case of the complexes with $P(OEt)_3$, suggesting that the coordination of Mn to the CN of the monocarbonyls can be destroyed by water.

TABLE 1. Analytical, IR, and ^{31}P NMR data

Compound	Analysis (calcd.)			IR (cm^{-1}) [b]		^{31}P NMR
	C	H	N	ν(CN) (m)	ν(CO) (s)	
$[Mn(CN)(CO)(bipy)\{P(OMe)_3\}_2]$ (**2a**)	41.2	5.0	8.3	2056	1841	176 [c,d,e]
	(42.1)	(5.1)	(8.2)			
$[Mn(CN)(CO)(Me_2\text{-bipy})\{P(OMe)_3\}_2]$ (**2b**)	40.8	5.1	6.9 [a]	2054	1840	178 [f]
	(40.3)	(5.1)	(6.7)			
$[Mn(CN)(CO)(bipy)\{P(OEt)_3\}_2]$ (**2c**)	48.0	5.9	7.0	2053	1837	173 [c,e]
	(48.2)	(6.4)	(7.0)			
$[Mn(CN)(CO)(Me_2\text{-bipy})\{P(OEt)_3\}_2]$ (**2d**)	48.3	6.5	6.7	2051	1832	175 [e,f]
	(49.3)	(6.7)	(6.7)			
$[Mn(CN)(CO)(bipy)\{P(OPh)_3\}_2]$ (**2e**)	65.1	4.4	4.5	2067	1876	157 [d,e]
	(65.1)	(4.3)	(4.7)			
$[Mn(CN)(CO)(Me_2\text{-bipy})\{P(OPh)_3\}_2]$ (**2f**)	64.6	4.8	4.5	2066	1869	158 [d,f]
	(65.7)	(4.6)	(4.6)			
$[Mn(CNMe)(CO)(bipy)\{P(OMe)_3\}_2]PF_6$ (**3a**)	34.5	4.0	6.5	2114	1880	172 [c]
	(33.9)	(4.3)	(6.2)			
$[Mn(CNMe)(CO)(Me_2\text{-bipy})\{P(OMe)_3\}_2]PF_6$ (**3b**)	36.6	4.4	6.4	2112	1878	171 [e,f]
	(36.0)	(4.7)	(6.0)			
$[Mn(CNMe)(CO)(bipy)\{P(OEt)_3\}_2]PF_6$ (**3c**)	39.3	5.2	5.3	2110	1874	167 [b]
	(39.7)	(5.4)	(5.6)			
$[Mn(CNMe)(CO)(Me_2\text{-bipy})\{P(OEt)_3\}_2]PF_6$ (**3d**)	41.1	5.3	5.6	2104	1873	168 [c,f]
	(41.3)	(5.7)	(5.4)			
$[Mn(CNMe)(CO)(bipy)\{P(OPh)_3\}_2]PF_6$ (**3e**)	55.6	4.1	4.6	2137	1906	156 [e,d]
	(56.2)	(3.9)	(4.1)			

[a] Calculated for the 1:1 CH_2Cl_2 solvate. [b] In CH_2Cl_2 solution, m = medium, s-strong. [c] In CH_2Cl_2 at room temperature. [d] CH_2Cl_2 at −50°C. [e] $CDCl_3$ at room temperature. [f] $CDCl_3$ at −50°C.

TABLE 2. ^{1}H and ^{13}C NMR data

Compound	^{1}H NMR	^{13}C NMR
fac-[Mn(CN)(CO)$_3$(bipy)] (**1a**)	9.06 (2H); 8.18 (2H); 7.99 (2H); 7.52 (2H) [a]	222.3 (br, 2C, CO); 214.0 (br, 1C,CO); 161.0 (br, CN), 155.8, 154.0, 139.0, 127.1, 123.3 (bipy) [a]
fac-[Mn(CN)(CO)$_3$(Me$_2$-bipy)] (**1b**)	8.88 (2H); 7.92 (2H); 7.27 (2H); 2.50 (6H, Me) [a]	221.5 (2C, CO); 213.2 (1C, CO); 155.9 (CN); 154.6, 152.7, 151.0, 127.8, 123.9 (bipy); 21.8 (Me) [c]
[Mn(CN)(CO)(bipy){P(OMe)$_3$}$_2$] (**2a**)	9.94 (d, 1H); 9.30 (d, 1H); 8.04 (d, 1H); 7.89 (m, 2H); 7.56 (t, 1H); 7.43 (t, 1H); 7.04 (t, 1H) (bipy); 3.41 (t, 18H, OMe) [a]	231 (CO); 165 (CN); 157.3, 155.6, 155.4, 155.1, 135.4, 132.9, 123.9, 123.3, 121.2, 120.7 (bipy); 52.1 (OMe) [a]
[Mn(CN)(CO)(bipy){P(OEt)$_3$}$_2$] (**2c**)	9.89 (1H); 9.2 (1H); 8.00, 7.89, 7.82, 7.38, 7.04 (m, 6H) (bipy); 3.83 (12H, OCH_2CH$_3$); 0.95 (18H, OCH$_2$$\mathit{CH}_3$) [a]	227 (br, CO); 162 (br, CN); 158.4 br, 156.0br, 155.2br, 154.5br, 134.5, 133.4br, 123.6, 121.6br, 120.2, 120.1br (bipy); 60.8 (OCH_2CH$_3$); 16.7 (OCH$_2$$\mathit{CH}_3$) [a]
[Mn(CN)(CO)(bipy){P(OPh)$_3$}$_2$] (**2e**)	9.60 (1H); 8.83 (1H); 7.73 (d,d); 7.52, 7.26, 7.05, 6.94, 6.86, 6.58 (42H) (bipy and Ph) [b]	232 (br, CO); 168 (br, CN); 157.2, 156.2, 155.6, 155.5, 136.2, 134.3, 124, 120.9 (bipy); 152.8 (C$_1$); 130 (C$_2$); 124.6 (C$_4$); 121.4 (C$_3$, Ph) [a]
[Mn(CNMe)(CO)(bipy){P(OMe)$_3$}$_2$]PF$_6$ (**3a**)	9.14 (2H); 8.27 (2H); 8.06 (1H); 7.93 (1H); 7.59 (1H); 7.34 (1H) (bipy); 3.61 (3H, CNMe); 3.37 (t, 18H, OMe) [a]	227 (br, CO); 179 (br, CN); 156.8, 156.2, 155, 154.5, 138, 137.1, 126, 125.4, 122.7 (2C) (bipy); 52.7 (t, OMe); 32.3 (CNMe) [a]
[Mn(CNMe)(CO)(Me$_2$-bipy){P(OMe)$_3$}$_2$]PF$_6$ (**3b**)	8.94 (2H); 8.02 (2H); 7.4 (1H); 7.12 (1H) (bipy); 3.60 (3H, CNMe); 3.36 (18H, OMe); 2.54 (6H, *Me*$_2$-bipy) [b]	227 (br, CO); 180 (br, CN); 155.8, 155.3, 153.7, 153.2, 149.6, 148.7, 126.4, 126, 122.7, 122.6 (bipy); 51.9 (t, OMe); 31.3 (CNMe); 21, 20.9 (*Me*$_2$-bipy) [a]
[Mn(CNMe)(CO)(bipy){P(OEt)$_3$}$_2$]PF$_6$ (**3c**)	9.1 (2H); 8.27 (2H); 8.01 (1H); 7.88 (1H); 7.84 (1H); 7.63 (1H); 7.27 (1H, bipy); 3.7 (12H, OCH_2CH$_3$); 3.6 (3H, CNMe); 0.99 (18H, OCH$_2$$\mathit{CH}_3$) [a]	227 (br, CO); 181 (br, CN); 156.4, 155.8, 154.6, 153.9, 137.2, 136.2, 125.3, 124.8, 121.9, 121.8 (bipy); 61.1 (OCH_2CH$_3$); 31.6 (CNMe); 16.2 (OCH$_2$$\mathit{CH}_3$)
[Mn(CNMe)(CO)(Me$_2$-bipy){P(OEt)$_3$}$_2$]PF$_6$ (**3d**)	8.9 (m, 2H); 8.0 (d, 2H); 7.3 (d, 1H); 7.1 (d, 1H) (bipy); 3.71 (m, 12H, OCH_2CH$_3$); 3.55 (3H, CNMe); 2.56, 2.52 (6H, *Me*$_2$-bipy); 0.99 (t, 18H, OCH$_2$$\mathit{CH}_3$) [a]	227 (br, CO); 183 (br, CN); 156.4, 155.9, 154.3, 153.7, 149.7, 148.8, 126.7, 126.3, 122.9 (2C) (μ_2-bipy); 61.3 (OCH_2CH$_3$); 31.9 (CNMe); 21.6, 21.4 (*Me*$_2$-bipy); 16.6 (OCH$_2$$\mathit{CH}_3$) [a]
[Mn(CNMe)(CO)(bipy){P(OPh)$_3$}$_2$]PF$_6$ (**3e**)	8.86 (1H); 8.75 (1H); 8.05 (2H); 8.0 (2H); 7.31, 7.13, 7.1, 6.71, 6.68 (32H) (bipy and Ph); 2.96 (3H, CNMe) [b]	226 (br, CO); 173 (br, CN); 156.3, 155.7, 155, 154.2, 138.3, 137.4, 126.2, 125.3, 122.7 (2C) (bipy) [e]; 151.6 (C$_1$) [d]; 130.1 (C$_2$); 125.1 (C$_4$); 120.2 (C$_3$) (Ph); 31.3 (CNMe) [a]

[a] CD$_2$Cl$_2$ at room temperature. [b] CDCl$_3$. [c] CH$_2$Cl$_2$ at −80°C. [d] In CDCl$_3$ is a pseudotriplet centred at 151.9. [e] In CDCl$_3$ is split into two very close signals.

ligands are equivalent, whereas the two rings of the NN chelate are non-equivalent, two conditions that only occur in the isomer with the two $P(OR)_3$ *trans* to each other, and two different ligands *trans* to each N atom.

The room temperature ^{31}P NMR spectra of all the complexes (Table 1) consist of a very broad singlet, that when measured at *ca.* −50 to −80°C was much sharper but without a significant change in the chemical shifts. It has been repeatedly observed that signals corresponding to phosphites coordinated to manganese ($I = 5/2$) tend to be very broad at room temperature, particularly when there are *N*-donors present in the complexes.

The non-equivalence of the two rings of the NN chelate were shown by the complexity of the relevant ^{31}C NMR and ^{1}H NMR signals. In the case of the complex **2a**, 5 pairs of very close signals were observed in the ^{13}C NMR spectrum for the carbons of the bipyridine, and the ^{1}H NMR spectrum shows seven multiplets (one of intensity double that of the others) in the bipy region, while in both spectra, the signals of the two $P(OMe)_3$ clearly indicate their equivalence. The spectra of the $P(OEt)_3$ and $P(OPh)_3$, derivatives **2c** and **2e**, are similar (in the ^{13}C NMR spectrum of **2e** two of the twin signals of the bipy were masked by the signals of the C_6H_5 carbons of the phosphite). However, we observed that in the ^{13}C NMR spectrum of **2c** one of the two sets of signals of the bipy carbons is much broader than the other and is more sensitive to the pulse delay used for the NMR experiment. This suggests a difference in the T_2 relaxation time between the carbon atoms of the two rings of the bipyridine, probably caused by quadrupole effects of the N atoms.

The formation of the cyano-monocarbonyls **2** from the tricarbonyls *fac*-$[Mn(CN)(CO)_3(NN)]$ (**1**) implies a change in the position of the CN ligand with respect to the two N atoms of the chelating diimine (see Scheme 1). This unexpected effect can be accounted for by considering the characteristics of the CO-substitution reactions in manganese carbonyls having NN chelating ligands [3]. Although for L = $P(OEt)_3$ and $P(OMe)_3$, the intermediate carbonyl species could not be identified unambiguously by monitoring the reactions (i) by IR spectroscopy, in the case of NN = bipy and L = $P(OPh)_3$, the known [8] neutral cyanide complex *cis-trans*-$[Mn(CN)(CO)_2(bipy)\{P(OPh)_3\}]$ (**I1**) was clearly observed (the analogous dicarbonyls with alkyl phosphites are not known). We checked that the irradiation of **I1** with $P(OPh)_3$ in CH_2Cl_2 gave the monocarbonyl $[Mn(CN)(CO)(bipy)\{P(OPh)_3\}_2]$ obtained from the *fac*-$[Mn(CN)(CO)_3(bipy)]$. This suggests that the reaction (i) may follow the path (1a), (1b), (ic) in Scheme 1. The reaction (ia) is to be expected, taking into account that the CO's *cis* to both N atoms of the NN ligands are labile [3]. In this case, reaction (ib) would give the monocarbonyls $[Mn(CN)(CO)(NN)L_2]$ (**I2**), but, these would subsequently isomerize to the observed product **2**. However, with our data it was not possible to exclude other reaction pathways involving other dicarbonyl intermediates, and, furthermore, the formation of **2** from **1** could occur without the intermediacy of any other monocarbonyl. In fact, in many of the ligand-substitution reactions of octahedral manganese carbonyl complexes, the position of the entering ligands in the products does not reflect the position of the displaced ligands [3].

On the other hand, we observed that the cyano-monocarbonyl $[Mn(CN)(CO)(bipy)L_2]$ for $P(OEt)_3$ was quickly formed upon UV irradiation of the corresponding [6] cationic dicarbonyl *cis-trans*-$[Mn(CO)_2(bipy)L_2]ClO_4$ (**4**) in the presence of [PPN]CN (reaction (ii) in Scheme 1) (with KCN the reaction was much slower and accompanied by decomposition). Considering the structure of the neutral cyano-carbonyl **2**, this reaction is totally analogous to the reaction of **4** with phosphites under UV irradiation to give *mer*-$[Mn(CO)(NN)L_3]ClO_4$ [6].

The cyano-monocarbonyls $[Mn(CN)(CO)(NN)L_2]$ (**2**) are very reactive species, and similarly to other cyanodi- and mono-carbonyls of manganese [7,8], they react with MeI in THF in the presence of KPF_6, (reaction (iii) in Scheme 1) to give the cationic methylisocyanide cationic complexes *trans*-$[Mn(CNMe)(CO)(NN)L_2]PF_6$ (**3a–3e**) characterized by the data in Tables 1 and 2. The salts **3** are purple crystalline solids (orange for $P(OPh)_3$), and are stable, specially in the solid state (the decomposition of the $P(OPh)_3$ derivative in solution was slightly faster).

All the compounds **3** have molar conductivities in a 5×10^{-4} M acetone solution of the order of 120 Ω^{-1} cm^2 mol^{-1}, and their spectroscopic properties are consistent with the structures shown in Scheme 1. Thus, all the ^{31}P NMR spectra showed a singlet (much broader at room temperature) indicating that both phosphorus atoms are equivalent. (As a comparison, the ^{31}P NMR spectrum of *cis-trans*-$[Mn(CO)_2(bipy)\{P(OEt)_3\}_2]PF_6$ shows a very broad singlet centred at 159.6, while the that of the *cis-cis* isomer shows two broad signals of equal intensity at 177.3 and 150.3 ppm. As in the case of the neutral derivative **2a**, the ^{1}H NMR spectrum of **3a** and **3b** show a second order "deceptively simple" triplet of a $X_9AA'X'_9$ spin system, and therefore consistent with *trans* phosphites. Finally, the ^{13}C NMR spectrum of the bipy derivatives **3a**, **3c**, and **3e**, show only one singlet for the methyl carbon of the MeNC, but 5 pairs of very close singlets for the rings carbon atoms, and the spectra of **3b** and **3d** also show two different signals for the methyl groups of the 4-4′-dimethylbipyridine indicating the non-equivalence of the two positions *trans* to the two nitrogen atoms [as a comparison, the ^{31}C NMR spectrum of *cis-trans*-[Mn-(CO)$_2$(bipy){P(OEt)$_3$}$_2$]PF$_6$ shows the following signals: 224.0 (br, CO), 155.8, 154.1, 138.5, 126.1, 122.6 (bipy), 62.0 (O–CH$_2$–), and 16.1 (–CH$_3$) ppm.

The formation of the cationic complexes **3** from the reaction of the neutral cyanide derivatives **2** with MeI and KPF$_6$ shows that this reaction occurs under kinetic control with retention of stereochemistry. Similar results have been previously observed with the cyanide complexes *cis*- and *trans*-[Mn(CN)(CO)$_2$(dppm){P(OPh)$_3$}] [7], *trans*-[Mn(CN)(CO)(dppm)$_2$] [7], and *cis-trans*-[Mn(CN)(CO)$_2$(bipy){P(OPh)$_3$}] [8], that react with MeI to give the corresponding cationic isocyanide derivatives without stereochemical changes.

The cyanocarbonyls **2** also react readily with HCl(g), to give the corresponding bright red cationic complexes containing CNH as a ligand, and with BH$_3$(thf) to give the red, neutral derivatives with a coordinated CNBH$_3$. However, these products were too unstable to be isolated, and revert very quickly to the starting materials.

3. Experimental part

All reactions were carried out under N$_2$, using purified and dried solvents. The IR spectra were recorded with a Perkin-Elmer FT 1720-X spectrometer. The NMR spectra were recorded on a Bruker AC-200, and AC-300 instruments. The ^{1}H and ^{13}C NMR spectra are quoted in ppm relative to TMS, and the ^{31}P NMR spectra are in ppm relative to external 85% aqueous H$_3$PO$_4$. Magnetic measurements (Faraday method) were made with a Bruker BE-15 balance. The compounds *fac*-[Mn(CN)(CO)$_3$(NN)] for NN = bipy (**1a**), and 4-4′-dimethylbipyridine (**1b**), were prepared by a modification of the method described elsewhere [8] (see below).

3.1. Preparation of fac-[Mn(CN)(CO)$_3$(4-4′-Me$_2$-bipy)] (1b)

To a solution of *fac*-[MnBr(CO)$_3$(4-4′-Me$_2$-bipy)] (0.4 g, 0.99 mmol) in CH$_2$Cl$_2$ (15 ml), was added solid AgCN (0.16 g, 1.19 mmol) and the mixture was stirred overnight at room temperature in the dark. The resulting solution was filtered, washed with a concentrated aqueous solution of sodium thiosulphate, dried with solid sodium sulphate, filtered again, and concentrated *in vacuo* to *ca.* 5 ml. Addition of hexane (40 ml) with stirring gave a dark yellow solid that was recrystallized from CH$_2$Cl$_2$/hexane. Yield 0.3 g. (90%).

IR in CH$_2$Cl$_2$: 2113w, 2028s, 1936s cm^{-1} (NMR data in Table 2).

3.2. Preparation of cis-trans-[Mn(CN)(CO)(NN)L$_2$] (2)

The following preparation for **2e** is totally representative of all the other complexes, but, because the actual reaction times depend on the scale and the UV equipment, and the prolonged irradiation may increase the decomposition, in all cases (particularly in the scaling up) it is advisable to check by IR spectroscopy when the ν(CO) absorptions of the starting *fac*-tricarbonyl have disappeared. In this respect, the more useful band at higher frequency (2030 for **1a** and 2028 for **1b**), because there are other broad absorptions in the region around 1930–1940 cm^{-1} (from the phosphites in a large excess) that cannot be removed by longer irradiation and that disappear during the purification process.

A magnetically stirred solution of the complex *fac*-[Mn(CN)(CO)$_3$(bipy)] (0.14 g, 0.44 mmol) and P(OMe)$_3$ (1 ml) in CH$_2$Cl$_2$ (15 ml) was irradiated with UV light at *ca.* −12°C for 45 min. The black-green solution was evaporated *in vacuo*. The residue was washed three times with hexane (40 ml) to remove most of the excess P(OMe)$_3$, and dissolved in CH$_2$Cl$_2$. The solution was vigorously stirred with 25 ml of degassed water (three times), and dried with Na$_2$SO$_4$. The resultant solution was concentrated to *ca.* 5 ml, mixed with hexane (30 ml) and concentrated again *in vacuo* until a dark green solid was precipitated. The product was recrystallized in the same manner from CH$_2$Cl$_2$/hexane to give **2a** as a black-green microcrystalline powder. Yield: 0.16 g, 0.31 mmol (70.9%).

3.3. Preparation of cis-trans-[Mn(CNMe)(CO)(NN)-L$_2$]PF$_6$ (3)

The following preparation for **3b** is representative of all the other complexes.

To a solution of *cis-trans*-[Mn(CN)(CO)(bipy){P-(OMe)$_3$}$_2$] (0.1 g, 0.19 mmol) in THF (15 ml) were added MeI (1 ml) and solid KPF$_6$ (0.5 g), and the mixture was stirred for 24 h at room temperature in the dark (precautions should be taken to prevent the evaporation of the MeI). The mixture was dried *in vacuo* and washed once with diethyl ether (15 ml). The crude product was dissolved in CH$_2$Cl$_2$, filtered and mixed with enough diethyl ether to give a small amount of a dark precipitate and a dark red solution that was concentrated, mixed with hexane and kept in a freezer for several hours to give a purple crystalline solid, that was recrystallized from CH$_2$Cl$_2$/hexane. Yield: 0.09 g, 0.13 mmol (70%).

The compound **3e** is dark orange, and the yield is usually smaller.

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