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CATIONIC CARBONYL COMPLEXES OF MANGANESE(I) WITH DIPHENYLPHOSPHINE

G. A. CARRIEDO, V. RIERA,* M. L. RODRÌGUEZ and J. J. SAINZ-VELICIA

Departamento de Química Organometálica, Universidad de Oviedo, 33071 Oviedo, Spain

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Abstract—The cationic complexes $[Mn(CO)_{6-n}(PHPh_2)_n]ClO_4$, for $n = 1$ to 4 and $[Mn(CO)_{4-n}(\overset{\frown}{L\,L})(PHPh_2)_n]A$ ($\overset{\frown}{L\,L}$ = dppm or dppe, $n = 1$, A = ClO_4; $\overset{\frown}{L\,L}$ = bipy or phen, $n = 1$ or 2, A = ClO_4 or PF_6) have been prepared from $PHPh_2$ and $Mn(OClO_3)(CO)_5$ or *fac*-$MnX(CO)_3(\overset{\frown}{L\,L})$ respectively (X = Br or $OClO_3$). The *fac*-tricarbonyls *fac*-$[Mn(CO)_3(PHPh_2)_3]ClO_4$ and *fac*-$[Mn(CO)_3(\overset{\frown}{L\,L})(PHPh_2)]ClO_4$ for $\overset{\frown}{L\,L}$ = dppm or dppe, isomerize upon heating to the corresponding *mer*-tricarbonyls, and the dicarbonyl *cis*-$[Mn(CO)_2(PHPh_2)_4]ClO_4$ gives the *trans* isomer under UV irradiation.

It is known that the reaction of the neutral perchlorate complex $Mn(OClO_3)(CO)_5$ with monodentate ligands (L) gives $[Mn(CO)_5L]ClO_4$ or *fac*-$[Mn(CO)_3L_3]ClO_4$, and that, in the case of the phosphites $[P(OR)_3]$, the more substituted products $[Mn(CO)_2L_4]ClO_4$ can be obtained.[1] The tetracarbonyls $[Mn(CO)_4L_2]ClO_4$ were not made from $Mn(OClO_3)(CO)_5$, but the BF_4 salts can be prepared by other routes.[2] We have found that the reaction of the secondary phosphine $PHPh_2$ with $Mn(OClO_3)(CO)_5$ leads to the cationic carbonyl complexes $[Mn(CO)_{6-n}(PHPh_2)_n]ClO_4$ for $n = 1$ to 4 by varying the reaction conditions. Herein we describe the preparation of those complexes and of the related species $[Mn(CO)_{4-n}(\overset{\frown}{L\,L})(PHPh_2)_n]A$, where for $\overset{\frown}{L\,L}$ = dppm† or dppe, $n = 1$ and for $\overset{\frown}{L\,L}$ = bipy or phen $n = 1$ or 2 and A = ClO_4 or PF_6.

EXPERIMENTAL

All reactions were carried out under dry, oxygen-free argon. The NMR spectra were recorded with a JEOL FX 90Q instrument and the IR with a Perkin–Elmer 298 spectrometer. The compounds $Mn(OClO_3)(CO)_5$,[1] *fac*-$[Mn(OClO_3)(CO)_3(\overset{\frown}{L\,L})]$ ($\overset{\frown}{L\,L}$) = dppm or dppe,[9] $\overset{\frown}{L\,L}$ = bipy or phen[10] were prepared by published methods.

$[Mn(CO)_5(PHPh_2)]ClO_4$ (I)

A mixture of the complex $Mn(OClO_3)(CO)_5$ (0.32 g, 1 mmol) and the phosphine $PHPh_2$ (0.19 cm^3, 1 mmol) in dichloromethane (40 cm^3), was stirred for 17 h at room temperature and evaporated almost to dryness. The residue was washed repeatedly with diethyl ether and crystallized from $CH_2Cl_2 : Et_2O$ as a pale yellow microcrystalline solid (0.45 g, 86%). The compound was stored cooled and under dry argon

cis-$[Mn(CO)_4(PHPh_2)_2]ClO_4$ (II)

A mixture of $Mn(OClO_3)(CO)_5$ (0.22 g, 0.75 mmol) and $PHPh_2$ (0.39 cm^3, 2.24 mmol) in ethanol (8 cm^3) was refluxed for 75 min and cooled to room temperature. The white crystalline precipitate was separated from the mother liquor and recrystallized from $CH_2Cl_2 : Et_2O$ (0.32 g, 67.5%). From the mother liquor a mixture of **II** and **III** was obtained by concentrating and precipitating with ether.

fac-$[Mn(CO)_3(PHPh_2)_3]ClO_4$ (III)

A solution of $Mn(OClO_3)(CO)_5$ (0.4 g, 1.36 mmol) in acetone (15 cm^3) was refluxed for 90 min and allowed to cool to room temperature. To the resulting solution of *fac*-$[Mn(CO)_3(Me_2CO)_3]ClO_4$, the phosphine $PHPh_2$ (0.85 cm^3, 4.9 mmol) was added and the mixture was stirred for 2 h at room temperature. Part of the product precipitated as a

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* Author to whom correspondence should be addressed.

† Throughout this paper dppm = $Ph_2PCH_2PPh_2$, dppe = $Ph_2PCH_2CH_2PPh_2$, bipy = 2,2′-bipyridine and phen = 1,10-orthophenanthroline.

white solid. Excess of diethyl ether was added and the precipitate was separated and washed with ether. Recrystallization from $CH_2Cl_2:Et_2O$ gave white microcrystalline **III** (0.78 g, 72%).

Isomerization of **III**

The salt **III** (0.1 g, 0.125 mmol) was heated in refluxing *n*-butanol (10 cm^3) for 1 h and the resulting solution was allowed to cool to room temperature. Addition of a small amount of diethylether gave a first precipitate that was mainly the *mer* isomer (**V**), and from the mother liquor the remaining *fac*-tracarbonyl mixed with some **V** was precipitated with hexane.

cis-$[Mn(CO)_2(PHPh_2)_4]ClO_4$ (IV)

To a solution of **III** (0.10 g, 0.13 mmol) and $PHPh_2$ (0.1 cm^3, 0.57 mmol) in acetone (12 cm^3), freshly sublimed $ONMe_3$ (0.01 g, 0.13 mmol) was added and the mixture was stirred at room temperature for 5 h. The volatiles were removed *in vacuo* and the residue was washed with diethylether. The resulting solid was recrystallized from CH_2Cl_2: Et_2O as pale yellow microcrystals (0.06 g, 49%).

trans-$[Mn(CO)_2(PHPh_2)_4]ClO_4$ (VI)

A mixture of **III** (0.16 g, 0.2 mmol) and $PHPh_2$ (0.8 cm^3, 4.6 mmol) in CH_2Cl_2 (10 cm^3) was irradiated at −15°C until the IR of the solution no longer showed the $\nu(CO)$ absorptions of the starting material. The solution was concentrated to *ca.* 3 cm^3 and diethylether was added to give a pale yellow microcrystalline precipitate (0.1 g, 52%) that was recrystallized from $CH_2Cl_2:Et_2O$.

fac-$[Mn(CO)_3(\overset{\frown}{LL})(PHPh_2)]ClO_4$ (VII)

A solution of *fac*-$Mn(OClO_3)(CO)_3(dppe)$ (0.74 g, 1.16 mmol) and $PHPh_2$ (0.36 cm^3, 2.1 mmol) in CH_2Cl_2 (40 cm^3) was stirred for 7 h. The solvent was removed *in vacuo* and the residue was washed with ether. Recrystallization from $CH_2Cl_2:Et_2O$ gave pale yellow microcrystalline **VIIb** (0.88 g, 92.5%).

The other *fac*-tricarbonyls **VII** were similarly prepared from the corresponding *fac*-$[Mn(OClO_3)(CO)_3(\overset{\frown}{LL})]$ with the following reaction times and yields: $\overset{\frown}{LL}$ = dppm, 48 h, 61%; $\overset{\frown}{LL}$ = bipy, 17 h, 60% (made in acetone); $\overset{\frown}{LL}$ = phen, 16 h, 64% (made in acetone).

fac-$[Mn(CO)_3(bipy)(PHPh_2)]PF_6$ (VIIe)

A mixture of *fac*-$[MnBr(CO)_3(bipy)]$ (0.3 g, 0.8 mmol), $PHPh_2$ (0.24 cm^3, 1.38 mmol) and $TlPF_6$ (0.4 g, 1.14 mmol) in CH_2Cl_2 (15 cm^3) was stirred for 5 h at room temperature and filtered through celite. Evaporation of the solvent *in vacuo* gave an oil that was washed several times with hexane. Recrystallization from $CH_2Cl_2:Et_2O$ gave yellow–brown microcrystalline **VIIe** (0.49 g, 98%).

Isomerization of fac-$[Mn(CO)_3(\overset{\frown}{LL})(PHPh_2)]ClO_4$ ($\overset{\frown}{LL}$ = dppm *or* dppe)

The compound *fac*-$[Mn(CO)_3(dppm)(PHPh_2)]ClO_4$ (0.5 g, 0.62 mmol) was heated in refluxing *n*-butanol (25 cm^3) for 4.5 h and the mixture was cooled to room temperature. After concentrating (*in vacuo*) to half the volume, hexane was added and the yellow precipitate was washed with hexane to give 0.42 g of *mer*-$[Mn(CO)_3(dppm)(PHPh_2)]ClO_4$ mixed with some *cis*-$[Mn(CO)_2(dppm)_2]ClO_4$.

Similarly, the dppe compound gave a mixture of the corresponding *mer*-tricarbonyl and *trans*-$[Mn(CO)_2(dppe)_2]ClO_4$.

cis-trans-$[Mn(CO)_2(bipy)(PHPh_2)_2]PF_6$ (VIII)

A mixture of **VIIe** (0.10 g, 0.16 mmol) and $PHPh_2$ (0.05 cm^3, 0.29 mmol) in toluene (10 cm^3) was refluxed for 1 h and allowed to cool to room temperature. On standing an orange precipitate was formed that was recrystallized from $CH_2Cl_2:Et_2O$ (0.10 g, 78%).

RESULTS AND DISCUSSION

Stirring a 1:1 molar mixture of $Mn(OClO_3)(CO)_5$ and $PHPh_2$ in CH_2Cl_2 at room temperature (i in Scheme 1) gave the cationic pentacarbonyl $[Mn(CO)_5(PHPh_2)]ClO_4$ (**I**), characterized by the data in Tables 1 and 2. This compound could be purified by precipitation with Et_2O from CH_2Cl_2 solutions under argon, but when a solution in CH_2Cl_2:EtOH (free or $PHPh_2$) was concentrated by heating at reduced pressure, it was almost quantitatively transformed into the previously known dimer $[Mn_2(CO)_8(\mu\text{-}PPh_2)_2]$[3] with concomitant formation of CO and $HClO_4$, as evidenced by the strong acidity of the mother liquor. This decomposition also occurred by heating the pure cationic pentacarbonyl **I** in ethanol and also in CH_2Cl_2 solutions in the presence of H_2O* or

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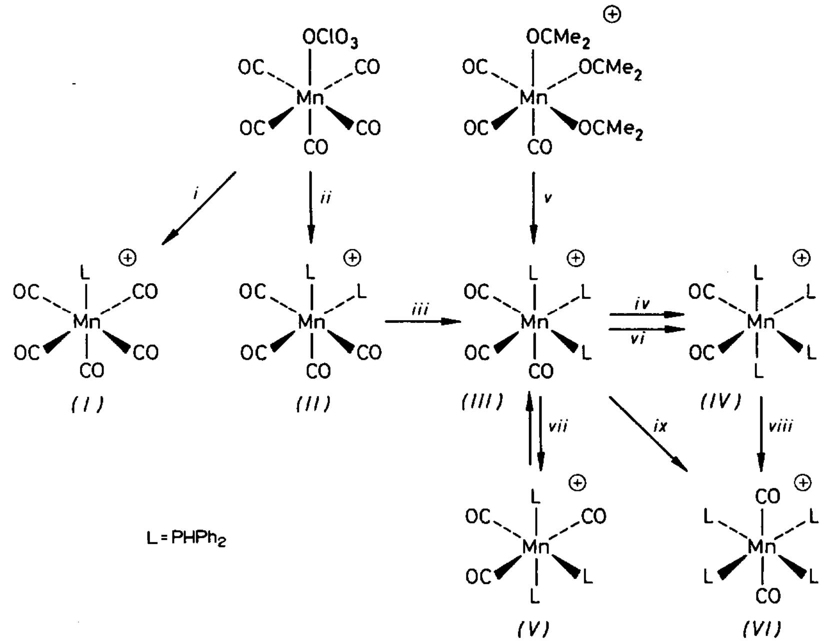
* The IR spectrum of **I** in CH_2Cl_2 solution was better obtained using CaF_2 windows. On some occasions when NaCl windows were used, particularly in the presence of water vapour, the formation of the dimer was observed, probably favoured by the heat of the IR source.



Scheme 1. Key to reagents and conditions. (i) $PHPh_2$ (1 : 1) in CH_2Cl_2 at room temperature, (ii), (iii) and (iv) $PHPh_2$ (excess) in refluxing ethanol, (v) $PHPh_2$ (3 : 1) in Me_2CO at room temperature, (vi) $PHPh_2$ (excess) and $ONMe_3$ in CH_2Cl_2 at room temperature, (vii) refluxing *n*-butanol, (viii) and (ix) in CH_2Cl_2 at −15°C with U.V. irradiation.

Na_2CO_3, although in the latter case the dimer was formed along with another red unidentified product. These transformations are clearly favoured by the stability of the diphenylphosphido bridged species, and by the enhanced acidity of the $PHPh_2$ ligand coordinated to the $Mn(CO)_5^+$ fragment. On the other hand, I reacted very quickly with Bu^n_4NBr in refluxing CH_2Cl_2 to give the known tetracarbonyl *cis*-$[MnBr(CO)_4(PHPh_2)]$,[3] indicating that one CO is labilized in the cationic pentacarbonyl.

The reaction of the perchlorate complex $Mn(OClO_3)(CO)_5$ with a two- or three-fold excess of $PHPh_2$ in refluxing ethanol (ii in the scheme) gave the tetracarbonyl *cis*-$[Mn(CO)_4(PHPh_2)_2]ClO_4$ (**II**) as a crystalline precipitate. The ^1H NMR of this compound in $CDCl_3$ solution showed a pattern consistent with an AA′XX′ system similar to that described for the analogous neutral molybdenum complex $Mo(CO)_4(PHPh_2)_2$.[4] In Table 2 only the centre of the multiplet and the separation (in Hz) between the two more intense signals (the external ones) are given. The preparation of the tetracarbonyl **II** by reaction of $PHPh_2$ with $Mn(OClO)_3(CO)_5$ is similar to the result obtained with the ligand tetramethylthiourea (TMTU),[5] but contrasts with the observation that the reaction of the perchlorate complex with other monodentate ligands gives the tricabonyls *fac*$[Mn(CO)_3L_3]ClO_4$, probably passing through the tetracarbonyls, although the latter are not detected by monitoring the reaction by IR.[1] In the reaction (ii in scheme) the *fac*-tricarbonyl *fac*-$[Mn(CO)_3(PHPh_2)_3]ClO_4$ (**III**) was also observed, but its formation from **II** (iii in Scheme) was slow in refluxing ethanol and on prolonged heating it was obtained together with some remaining **II** and the *cis*-dicarbonyl *cis*-$[Mn(CO)_2(PHPh_2)_4]ClO_4$ (**IV**). The latter compound could be prepared from the tricarbonyl **III** and excess of $PHPh_2$ in refluxing ethanol (iv in scheme) but only in poor yield because it had to be carefully crystallized out from the mixture before the reaction is completed otherwise some decomposition to an unidentified dicarbonyl begins.

The cationic tricarbonyl **III** could be conveniently obtained pure in good yield from $PHPh_2$ and *fac*-$[Mn(CO)_3(Me_2CO)_3]ClO_4$[1] in acetone (reaction v in the scheme). The dicarbonyl **IV** was easily prepared, also in good yield, by reacting **III** with $PHPh_2$ in CH_2Cl_2 in the presence of $ONMe_3$, (vi in scheme) a method often employed to promote CO substitution,[6] that in some cases has led to unexpected isomers.[7] Heating the *fac*-tricarbonyl **III** in refluxing *n*-butanol (viii in scheme) resulted in the formation of *mer*-$[Mn(CO)_3(PHPh_2)_3]ClO_4$ (**V**), as evidenced by the changes in the $\nu(CO)$ IR spectrum

Table 1. Melting point, conductivity, analytical and IR data for the compounds

Compound	M.p.[a] (°C)	Λ (Ω^{-1} cm^2 mol^{-1})[b]	Analysis [found (calc)%] C	H	N	IR (cm^{-1})[c] ν(CO)[d]
[Mn(CO)$_5$(PHPh$_2$)]ClO$_4$ (**I**)	80	120	42.8 (42.5)	2.46 (2.31)		2150m, 2102m, 2062s
cis-[Mn(CO)$_4$(PHPh$_2$)$_2$]ClO$_4$ (**II**)	186	136	52.7 (52.7)	3.46 (3.47)		2102m, 2037s, 2022s, 1999sh
fac-[Mn(CO)$_3$(PHPh$_2$)$_3$]ClO$_4$ (**III**)[e]	183	144	58.6 (58.8)	4.19 (4.14)		2038s, 1965s.br
cis-[Mn(CO)$_2$(PHPh$_2$)$_4$]ClO$_4$ (**IV**)	171	123	62.8 (62.9)	4.61 (4.61)		1964s, 1909s
trans-[Mn(CO)$_2$(PHPh$_2$)$_4$]ClO$_4$ (**VI**)	149	133	62.6 (62.9)	4.47 (4.61)		1916s[f]
fac-[Mn(CO)$_3$(dppm)(PHPh$_2$)]ClO$_4$ (**VIIa**)[g]	120	106	60.0 (59.4)	4.05 (4.11)		2030s, 1955s.br
fac-[Mn(CO)$_3$(dppe)(PHPh$_2$)]ClO$_4$ (**VIIb**)[h]	110	120	59.0 (59.8)	4.30 (4.29)		2033s, 1958s.br
fac-[Mn(CO)$_3$(phen)(PHPh$_2$)]ClO$_4$ (**VIIc**)	177[i]	132	53.0 (53.6)	3.09 (3.17)	4.49 (4.63)	2045s, 1970s, 1935s
fac-[Mn(CO)$_3$(bipy)(PHPh$_2$)]ClO$_4$ (**VIId**)	136[i]	140	50.7 (51.7)	3.19 (3.30)	4.67 (4.82)	2045s, 1972s, 1938s
fac-[Mn(CO)$_3$(bipy)(PHPh$_2$)]PF$_6$ (**VIIe**)	156[i]	125	47.3 (47.9)	3.28 (3.03)	4.15 (4.47)	2045s, 1972s, 1938s
cis-trans-[Mn(CO)$_2$(bipy)(PHPh$_2$)$_2$]PF$_6$ (**VIII**)	224	131	55.0 (55.1)	3.78 (3.82)	3.47 (3.57)	1952s, 1884s

[a] With decomposition.

[b] In 5×10^{-4} M acetone solution.

[c] In CH$_2$Cl$_2$ solution.

[d] The ν(PH) band could not be clearly observed. Ambiguities came because of the near coincidence with the CO$_2$ absorptions in this region.

[e] For the *mer* isomer ν(CO): 2040w, 1972s.br.

[f] ν(PH) at 2330 cm^{-1}.

[g] For the *mer* isomer ν(CO): 2050w, 1965s.br.

[h] For the *mer* isomer ν(CO): 2040w, 1960s.br.

[i] Before melting the colour changed from yellow to red.

[from two equally strong bands to one weaker than the other (Table 1)]. This process is similar to that observed in the case of many other cationic tricarbonyls with phosphorus ligands;[1] however, the isomerization could not be completed after prolonged heating and a mixture of the two isomers **III** and **V** was obtained. This suggests that at high temperatures, the equilibrium vii shown in the Scheme is established. The ^{31}P(^{1}H)NMR spectrum of **III** featured a very broad signal even at −90°C centred at *ca.* 33 ppm with $\Delta\nu_{1/2} = 750$ Hz. (920 Hz at −60°C) while the spectrum of the mixture having more of the *mer*-isomer taken at −60°C, showed also a doublet centred at 43.6 ppm and a triplet centred at 26.1 ppm with intensity ratio 2 : 1 and with ^2J(P,P) = 39 Hz. In the non-decoupled ^{31}P NMR spectrum the doublet centred at 43.7 ppm was split into two broad multiplets separated by *ca.* 360 Hz and the triplet was split into two broad multiplets separated by *ca.* 390 Hz. The ^{1}H NMR spectrum of **III** showed a complex multiplet centred at 6.43 ppm with a separation of 396 Hz between the two extreme and more intense peaks. In the ^{1}H NMR spectrum of the isomer mixture, two complex multiplets assignable to the *mer*-tricarbonyl were observed, one was centred at 6.35 ppm with a separation between the more intense peaks of 369 Hz but only half of the other multiplet (at 3.46 ppm) could be observed, the other half probably being hidden by the strong signal of the PPh$_2$ groups. All these features are consistent with the structures proposed for **III** and **V**.

The *cis*-dicarbonyl **IV** could be converted into the isomer *trans*-[Mn(CO)$_2$(PHPh$_2$)$_4$]ClO$_4$ (**VI**) by

Table 2. NMR data for the compounds

Compound	^{1}H NMR[a]	^{31}P{^{1}H} NMR[b]
I	7.53(413)	11(v.br.)[c]
II	7.41(417)	23
III	6.50(398)	33(v.br.)[d]
IV	6.80(370),[e] 5.89(350)[e]	53.4(2P, t, ^{1}J(PP) = 36, $PHPh_2$), 34.7(2P, t, ^{1}J(PP) = 36, $PHPh_2$)[f]
V	6.35(369), 5.63[g](390)	43.6(2P, d, ^{1}J(PP) = 39, $PHPh_2$), 26.1(1P, t, ^{1}J(PP) = 39, $PHPh_2$)
VI	6.46(382)	43.6
VIIb	[h]	66.6(2P, d, ^{1}J(PP) = 39, dppe), 33.1(1P, t, ^{1}J(PP) = 40, $PHPh_2$)
VIIe	[h]	39.9
VIII	6.23(351)[i]	54.4

[a] In $CDCl_3$ unless otherwise stated. Measured at room temp. in ppm with ref. to TMS. Only the centre of the multiplet corresponding to the $P\underline{H}Ph_2$ proton is quoted; in parentheses is given the separation between the two more intense peaks that corresponds closely to the ^{1}J(PH) coupling constant (in Hz).

[b] In CH_2Cl_2 solution measured at -60°C with reference to downfield of external 85% H_3PO_4 (in ppm). Coupling constants in Hz.

[c] $\Delta\nu_{1/2}$ *ca.* 1000 Hz.

[d] $\Delta\nu_{1/2} = 920$ Hz.

[e] Pseudotriplet with peak separation of *ca.* 8 Hz.

[f] The spectrum is in fact a AA′BB′ system, that has been measured directly from the spectrum as a first-order approximation.

[g] Estimated.

[h] Not observed because of the Ph protons.

[i] In d_6-acetone.

irradiating a CH_2Cl_2 solution with UV light at -15°C (viii in scheme), a reaction that resembles the UV promoted isomerization of the cationic dicarbonyl *cis*-$[Mn(CO)_2(dppm)_2]ClO_4$.[8] The spectroscopic data obtained for both isomeric dicarbonyls (Tables 1 and 2) were in accord with the structures proposed. The salt **VI** could be conveniently prepared directly from **III** and $PHPh_2$ under UV irradiation (ix in scheme).

Replacement of the coordinated $OClO_3$ ligand by $PHPh_2$ from the neutral complexes *fac*-$[Mn(OClO_3)(CO)_3(L\frown L)]$, gave the cationic carbonyls *fac*-$[Mn(CO)_3(L\frown L)(PHPh_2)]ClO_4$ [$L\frown L$ = dppm (**VIIa**), dppe (**VIIb**), phen (**VIIc**) or bipy (**VIId**)]. The analogous salt *fac*-$[Mn(CO)_3(bipy)(PHPh_2)]PF_6$ (**VIIe**) could be prepared directly from *fac*-$[MnBr(CO)_3(bipy)]$ and $PHPh_2$ in the presence of $TlPF_6$. Heating the *fac*-tricarbonyls containing the diphosphines resulted in the isomerization to the *mer*-tricarbonyls [ν(CO) IR: 2050 w, 1965 s.br (dppm) and 2040 w, 1960 s.br (dppe)]. This behaviour is similar to that observed for other cationic tricarbonyls with diphosphines,[9] however the *mer*-tricarbonyls with $PHPh_2$ were accompanied by the dicarbonyls *cis*-$[Mn(CO)_2(dppm)_2]ClO_4$ (in the case of the dppm complex) and *trans*-$[Mn(CO)_2(dppe)_2]ClO_4$ (in the dppe compound) and were not obtained pure.

By contrast, heating the *fac*-tricarbonyls with bipy or phen, resulted in decomposition giving the red dicarbonyls *cis-trans*-$[Mn(CO)_2(N\frown N)(PHPh_2)_2]ClO_4$ ($N\frown N$ = bipy or phen). This was confirmed by reacting the PF_6 salt **VIIe** with $PHPh_2$ in refluxing toluene that gave the complex *cis-trans*-$[Mn(CO)_2(bipy)(PHPh_2)_2]PF_6$ (**VIII**), characterized by the data in Tables 1 and 2 and that is analogous to other cationic *cis-trans* dicarbonyls with bipyridine or phenenthroline and two monodentate phosphorus ligands already known.[10]

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