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Formation and *fac-mer* isomerization of cationic phosphenium transition metal complexes formulated as $[\mathrm{M(bpy)(CO)_3}\{\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me}\}]^+$ (M = Cr, Mo, W) and $[\mathrm{M(dppe)(CO)_3}\{\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me}\}]^+$ (M = Mo, W)

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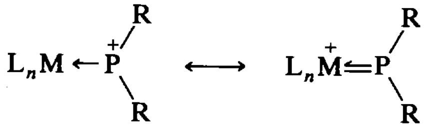
Abstract

In the reaction of $[\mathrm{M(bpy)(CO)_4}]$ (M = Cr, Mo, W) with $\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}$ under reflux with toluene or xylene, *fac*-$[\mathrm{M(bpy)(CO)_3}\{\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}\}]$ is prepared, which reacts with $\mathrm{BF_3 \cdot OEt_2}$ to give, by $\mathrm{OMe^-}$ abstraction from the phosphorus, a cationic phosphenium complex, *fac*-$[\mathrm{M(bpy)(CO)_3}\{\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me}\}]^+$. The facial isomer spontaneously isomerizes into its meridional form. The isomerization rate is in the order Cr > Mo > W. $[\mathrm{M(dppe)(CO)_3}\{\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}\}]$ (M = Mo, W), which is prepared from $[\mathrm{M(dppe)(CO)_3(NCMe)}]$ and $\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}$, also reacts with $\mathrm{BF_3 \cdot OEt_2}$ to give $[\mathrm{M(dppe)(CO)_3}\{\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me}\}]^+$, whose *fac-mer* isomerization is slower than that of the corresponding bpy complex.

Key words: Group 6; Phosphenium; Phosphite; Isomerism

1. Introduction

The coordination chemistry of cationic phosphenium ions, $\mathrm{PR_2^+}$, has recently attracted significant attention [1–5], because they have unique ligand behaviour towards transition metals due to the presence of both lone-pair electrons and a vacant p orbital on a phosphorus atom. Cationic phosphenium-transition metal complexes, $[\mathrm{L_nMPR_2}]^+$, can be described in the resonance forms below [6*].



The left form indicates that the cationic charge is located on the phosphorus, the P atom thus having a vacant p orbital. The right form represents the situation where sufficient electron density is offered by a filled d orbital of the transition metal to the vacant p orbital of the phosphorus, resulting in the location of the formal cationic charge on the transition metal. Thus, the complex can be seen, in an extreme case, to contain a double bond between the transition metal and the phosphorus.

Recently, we developed a new preparative method for $[\mathrm{Mo(bpy)(CO)_3}\{\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me}\}]^+$ (bpy = 2,2′-bipyridine) in which an OR group in $[\mathrm{Mo(bpy)(CO)_3}\{\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OR)}\}]$ is abstracted as an anion by boron trihalides such as $\mathrm{BF_3}$ or $\mathrm{BCl_3}$ [5b]. We report here the extension of this method to the Cr and W analogues and to $[\mathrm{M(dppe)(CO)_3}\{\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}\}]$ (M = Mo, W) (dppe = 1,2-bis(diphenylphosphino)ethane). We also report the *fac-mer* isomerization of the resulting cationic phosphenium complexes, which arises from the strong π-acceptability of the phosphenium ligand.

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* Reference number with an asterisk indicates a note in the list of references.

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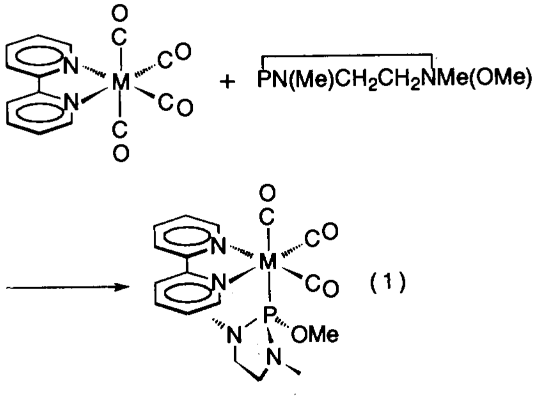
2. Results and discussion

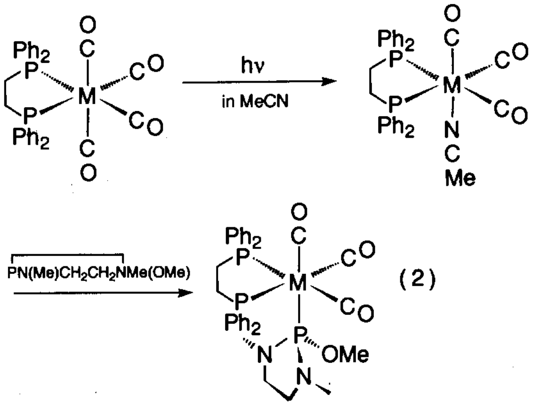
2.1. Preparation of *fac*-[M(bpy)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe(OMe)}] (M = Cr, Ia; Mo, IIa; W, IIIa) and *fac*-[M(dppe)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe(OMe)}] (M = Mo, IVa; W, Va)

The treatment of [M(bpy)(CO)$_4$] (M = Cr, Mo, W) with 1.5 equiv. of PN(Me)CH$_2$CH$_2$NMe(OMe) under toluene- or xylene-reflux conditions effected formation of *fac*-[M(bpy)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe(OMe)}] in a reasonable yield (eqn. (1)). The use of 1 equiv. of PN(Me)CH$_2$CH$_2$NMe(OMe) led to reduced yields of the products.



M = Cr : Ia 92%
Mo : IIa 65%
W : IIIa 61%

Neither thermal nor photo reactions of [M(dppe)(CO)$_4$] with PN(Me)CH$_2$CH$_2$NMe(OMe) were suitable for the synthesis of *fac*-[M(dppe)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe(OMe)}] (M = Mo, W), because of the formation of some unknown complexes in addition to *fac*- and *mer*-[M(dppe)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe(OMe)}], and moreover there was difficulty in isolating the *fac* form from the reaction mixture. Thus, IVa and Va were prepared under THF-reflux conditions from PN(Me)CH$_2$CH$_2$NMe(OMe) and [M(dppe)(CO)$_3$(NCCH$_3$)] obtained by a photoreaction of [M(dppe)(CO)$_4$] in CH$_3$CN (eqn. (2)).

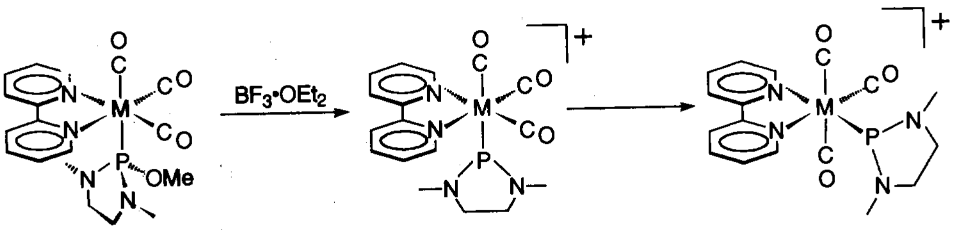


M = Mo : IVa 76%
W : Va 75%

Spectroscopic data of these complexes are summarized in Table 1. The ^{31}P NMR chemical shifts (126–147 ppm) fall in the range covered by diamino-substituted phosphites coordinating to a transition metal. For IVa and Va, the observation of one doublet and one triplet in ^{31}P NMR proves that these complexes have a facial configuration. In ^{1}H NMR, Ia, IIa, and IIIa show two multiplets assigned to CH$_2$ protons. The M–P bond may rotate freely, thus two multiplets can be attributed to the methylene protons close to and far from the OMe group.

2.2. Reaction of *fac*-[M(bpy)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe(OMe)}] (M = Cr, Ia; Mo, IIa; W, IIIa) with BF$_3$·OEt$_2$

A solution of *fac*-[M(bpy)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe(OMe)}] in CH$_2$Cl$_2$ was cooled to −78°C and BF$_3$·OEt$_2$ was added. The reaction mixture was allowed to warm to room temperature, and then the ^{31}P NMR spectrum was measured. The results are shown in Scheme 1, with ^{31}P NMR data in parentheses.



M = Cr : Ia (153.9)
Mo: IIa (138.0)
W : IIIa (129.8, J(PW)=334.6Hz)

Ib (263.8)
IIb (252.5)
IIIb (233.7, J(PW)=441.7Hz)

Ic (277.3)
IIc (268.2)
IIIc (242.6, J(PW)=561.1Hz)

Scheme 1.

In the reaction of the chromium complex Ia, the ^{31}P NMR spectrum of the resulting solution showed two signals at 263.8 and 277.3 ppm. These chemical shifts appearing in such a low field indicate the formation of the cationic phosphenium complexes, [Cr(bpy)(CO)$_3$-{PN(Me)CH$_2$CH$_2$NMe}]$^+$. Leaving the solution at room temperature caused an increase in intensity of the singlet at 277.3 ppm and the decrease of that at 263.8 ppm, and after several hours, the latter signal completely disappeared. The complex (Ic) thus remained finally in the solution, which showed the chemical shift at 277.3 ppm, was stable for several days at room temperature under a nitrogen atmosphere, though the IR spectrum could not be obtained due to decomposition in a KBr cell. The observation indicates a geometrical rearrangement taking place around the central Cr of the complex. In order to elucidate the geometrical structure of Ic, the ^{13}C NMR spectrum of the resulting solution was measured. In the region of carbonyl carbon, two doublets with similar coupling constants were observed ($\delta = 226.2$, d, J(CP) = 26.9 Hz, and $\delta = 219.9$, d, J(CP) = 22.0 Hz), and in the bpy region, ten singlets were detected. The observation clearly shows that Ic is [Cr(bpy)(CO)$_3${PN(Me)CH$_2$-CH$_2$NMe}]$^+$ with a meridional geometry. Therefore, the short-lived cationic phosphenium complex (Ib) showing a singlet at 263.8 ppm in ^{31}P NMR is reasonably assigned to *fac*-[Cr(bpy)(CO)$_3${PN(Me)CH$_2$-CH$_2$NMe}]$^+$ (*vide infra*).

A reaction of the molybdenum complex IIa gave similar results to those of the chromium complex. Two singlets were observed at 252.5 and 268.2 ppm for several hours after the reaction started, the latter signal increasing gradually in intensity at the expense of the former, and after one day only one singlet at 268.2 ppm was observed. Referring to the results of Cr and W (*vide infra*), we concluded that the chemical shifts at 252.5 and 268.2 ppm are due to *fac* (IIb) and *mer* (IIc) isomers of [Mo(bpy)(CO)$_3${PN(Me)-CH$_2$CH$_2$NMe}]$^+$, respectively.

In the case of the tungsten complex IIIa, the reaction mixture showed, in the ^{31}P NMR spectrum, only one singlet at 233.7 ppm accompanied by satellite peaks with the coupling constant of 441.7 Hz due to ^{183}W of 14.4% natural abundance. The low field chemical shift and the large coupling constant, together with the high IR frequencies of ν(CO) (2006, 1920, and 1868 cm^{-1}) compared with those of the starting complex, indicate the formation of [W(bpy)(CO)$_3${PN(Me)-CH$_2$CH$_2$NMe}]$^+$. The ^{13}C NMR spectrum of the solution showed two doublets due to the carbonyl carbons, of which one has a relatively large coupling constant (73.3 Hz) and the other a small one (14.7 Hz), and five singlets attributed to the bpy, indicating the formation

TABLE 1. Spectroscopic data

Complex	IR ν(CO) cm^{-1} (in CH$_2$Cl$_2$)	^{1}H NMR, ppm (in acetone-d_6)	^{31}P{^{1}H} NMR, ppm (in CH$_2$Cl$_2$)
fac-[Cr(bpy)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe(OMe)}] (Ia)	1911 1816 1786	9.45–7.38 (m, 8H, bpy) 3.11 (m, 2H, CH$_2$) 3.03 (d, J = 9.8 Hz, 3H, OCH$_3$) 2.82 (m, 2H, CH$_2$) 2.28 (d, J = 9.8 Hz, 6H, NCH$_3$)	153.9 (s)
fac-[Mo(bpy)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe(OMe)}] (IIa)	1916 1818 1790	9.19–7.51 (m, 8H, bpy) 3.10 (m, 2H, CH$_2$) 3.02 (d, J = 9.8 Hz, 3H, OCH$_3$) 2.81 (m, 2H, CH$_2$) 2.33 (d, J = 10.7 Hz, 6H, NCH$_3$)	138.0 (s)
fac-[W(bpy)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe(OMe)}] (IIIa)	1909 1814 1784	9.29–7.47 (m, 8H, bpy) 3.11 (m, 2H, CH$_2$) 3.01 (d, J = 9.8 Hz, 3H, OCH$_3$) 2.84 (m, 2H, CH$_2$) 2.30 (d, J = 10.8 Hz, 6H, NCH$_3$)	129.8 (J(PW) = 334.6 Hz)
fac-[Mo(dppe)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe(OMe)}] (IVa)	1944 1850	7.81–7.30 (m, 20H, Ph) 3.07–2.66 (m, 8H, NCH$_2$ and PCH$_2$) 2.93 (d, J = 10.3 Hz, 3H, OCH$_3$) 2.04 (d, J = 10.8 Hz, 6H, NCH$_3$)	146.5 (t, J(PP) = 33.6 Hz) 51.6 (d, J(PP) = 33.6 Hz)
fac-[W(dppe)(CO)$_3${PN(Me)CH$_2$CH$_2$NMe(OMe)] (Va)	1938 1842	7.81–7.28 (m, 20H, Ph) 3.08 (m, 4H, NCH$_2$ and PCH$_2$) 2.89 (d, J = 10.3 Hz, 3H, OCH$_3$) 2.79 (m, 4H, NCH$_2$ and PCH$_2$) 2.01 (d, J = 10.8 Hz, 6H, NCH$_3$)	126.8 (t, J(PP) = 25.8 Hz) (J(PW) = 338.2 Hz) 38.8 (d, J(PP) = 25.8 Hz) (J(PW) = 228.0 Hz)

of *fac*-$[W(bpy)(CO)_3\{PN(Me)CH_2CH_2NMe\}]^+$ (IIIb). The complex did not isomerize for several days at room temperature under a nitrogen atmosphere. After the complex had been refluxed in CH_2Cl_2 for 10 h, a small singlet appeared in ^{31}P NMR at 242.6 ppm accompanied by satellite peaks with $J = 561.1$ Hz, though the main signal was still a singlet at 233.7 ppm. The product formed by refluxing can be assigned to *mer*-$[W(bpy)(CO)_3\{PN(Me)CH_2CH_2NMe\}]^+$ (IIIc). The W complex is found to be much more inert towards geometrical rearrangement than the Cr and Mo complexes.

2.3. Reaction of fac-$[M(dppe)(CO)_3\{PN(Me)CH_2CH_2NMe(OMe)\}]$ (M = Mo, IVa; W, Va) with $BF_3 \cdot OEt_2$

In order to examine the effect of bpy on the *fac-mer* isomerization of cationic phosphenium complexes, Mo and W complexes containing dppe in place of bpy were prepared. A solution of IVa or Va in CH_2Cl_2 was cooled to −78°C and 2 equiv. of $BF_3 \cdot OEt_2$ was added. The solution was then allowed to warm to room temperature. The results obtained are shown in Scheme 2, together with ^{31}P NMR data in parentheses.

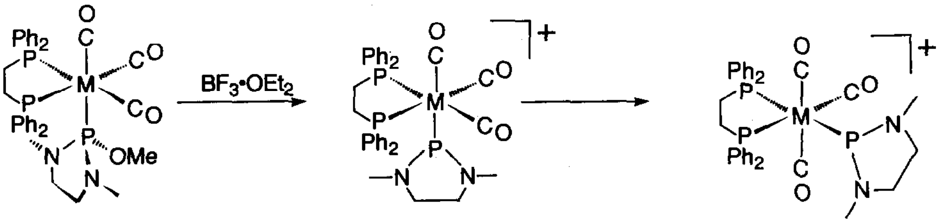
^{31}P NMR spectra of the resulting solutions exhibited a triplet at 282.4 ppm with $J(PP) = 29.0$ Hz and a doublet at 52.3 ppm with $J(PP) = 29.0$ Hz for the Mo complex, and a triplet at 257.1 ppm with $J(PP) = 22.1$ Hz, $J(PW) = 419.1$ Hz and a doublet at 38.5 ppm with $J(PP) = 22.1$ Hz, $J(PW) = 228.0$ Hz for the W complex. From the coupling pattern and coupling constants, the formation of *fac*-$[Mo(dppe)(CO)_3\{PN(Me)CH_2CH_2NMe\}]^+$ (IVb) and *fac*-$[W(dppe)(CO)_3\{PN(Me)CH_2CH_2NMe\}]^+$ (Vb) was deduced.

IVb and Vb remained stable in the solution for several days unless exposed to air, though they could not be isolated in the solid state. They slowly isomerize from the facial form to the meridional form. After 30 days, the ^{31}P NMR spectrum of the Mo complex showed an ABX pattern (283.4 ppm with $J(PP) = 119.0$ and 27.5 Hz, 55.9 ppm with $J(PP) = 27.5$ and 12.2 Hz, and 53.0 ppm with $J(PP) = 119.0$ and 12.2 Hz), assigned to *mer*-$[Mo(dppe)(CO)_3\{PN(Me)CH_2CH_2NMe\}]^+$ (IVc), together with the signals due to IVb. The IVc/IVb ratio was about 1/10. The ^{31}P NMR spectrum of the W complex after 30 days showed ABX pattern (256.1 ppm with $J(PP) = 114.0$ and 19.0 Hz, $J(PW) = 488.5$ Hz, 41.1 ppm with $J(PP) = 19.0$ Hz, $J(PW) = 224.3$ Hz and 36.8 ppm with $J(PP) = 114.0$ Hz, $J(PW) = 235.1$ Hz), assigned to *mer*-$[W(dppe)(CO)_3\{PN(Me)CH_2CH_2NMe\}]^+$ (Vc), together with the signals due to Vb. The Vc/Vb ratio was about 1/10.

2.4. Fac-mer isomerization of $[M(bidentate)(CO)_3\{PN(Me)CH_2CH_2NMe\}]^+$ (bidentate = bpy and dppe)

In the reaction of *fac*-$[M(bidentate)(CO)_3\{PN(Me)CH_2CH_2NMe(OMe)\}]$ with $BF_3 \cdot OEt_2$, it was found that the OMe group on the phosphorus is abstracted as an anion to give a cationic phosphenium complex, $[M(bidentate)(CO)_3\{PN(Me)CH_2CH_2NMe\}]^+$, the facial form of which is a kinetic product and the meridional form is a thermodynamic one. The isomerization rate is in the order of Cr > Mo > W, and becomes slower on going from bpy to dppe as a bidentate ligand on the transition metal. These cationic phosphenium complexes were stable in solution unless exposed to air, but several trials to isolate them in the solid state were unsuccessful.

The thermodynamic stability of the *mer* isomers over the *fac* isomers can be explained in terms of a strong π-acceptability of the cationic phosphenium ligand and from a filled d orbital of a transition metal. The



M = Mo : IVa (146.5, t, J(PP)=33.6Hz)
(51.6, d, J(PP)=33.6Hz)

IVb (282.4, t, J(PP)=29.0Hz)
(52.3, d, J(PP)=29.0Hz)

IVc (283.4, dd, J(PP)=119.0 & 27.5Hz)
(55.9, dd, J(PP)=27.5 & 12.2Hz)
(53.0, dd, J(PP)=119.0 & 12.2Hz)

W : Va (126.8, t, J(PP)=25.8Hz)
(J(PW)=338.2Hz)
(38.8, d, J(PP)=25.8Hz)
(J(PW)=228.0Hz)

Vb (257.1, t, J(PP)=22.1Hz)
(J(PW)=419.1Hz)
(38.5, d, J(PP)=22.1Hz)
(J(PW)=228.0Hz)

Vc (256.1, dd, J(PP)=114.0 & 19.0Hz)
(J(PW)=488.5Hz)
(41.1, d, J(PP)=19.0Hz)
(J(PW)=224.3Hz)
(36.8, d, J(PP)=114.0Hz)
(J(PW)=235.1Hz)

Scheme 2.

phosphenium ligand can accept more π-back donation in the *mer* isomer than in the *fac* isomer because the phosphenium ligand is *trans* to bpy in the *mer* isomer and is *trans* to the CO ligand, also requiring strong π-back donation, in the *fac* isomer. This is supported by the ν(CO) data in the IR spectra for both Mo and W complexes. The absorptions were observed in higher frequency for cationic phosphenium complexes compared with the starting phosphite complexes. Among these phosphenium complexes, the *fac* isomers showed the absorptions to be at frequencies higher by about 50 cm^{-1} than in the corresponding *mer* isomers. Another support is the coupling constant between the phosphenium phosphorus and ^{183}W. The constants are more than 100 Hz, and 70 Hz greater for the *mer* isomer than for the *fac* isomer of $[W(bpy)(CO)_3\{PN(Me)CH_2CH_2NMe\}]^+$ and $[W(dppe)(CO)_3\{PN(Me)CH_2CH_2NMe\}]^+$, respectively. This indicates that the double bond character between P and W, in other words, the extent of π-back donation from W to P, is greater in the *mer* isomer than in the *fac* isomer. Irrespective of the kind of Group 6 transition metals, ^{31}P NMR chemical shifts of phosphenium phosphorus of $[M(bpy)(CO)_3\{PN(Me)CH_2CH_2NMe\}]^+$ are observed in a lower field (by 13.5 ppm (Cr), 15.7 ppm (Mo), and 8.9 ppm (W)) for the *mer* isomers than for the *fac* isomers. Since the phosphenium ligand in the *mer* isomer may have more π-back donation than that in the *fac* isomer, the observed chemical shift changes are opposite to what is expected. It may be due to magnetic anisotropy of the bipyridine ligand and/or the central transition metal. For $[M(dppe)(CO)_3\{PN(Me)CH_2CH_2NMe\}]^+$ (M = Mo, W), the ^{31}P NMR chemical shifts of the phosphenium phosphorus are almost identical for the *fac* and *mer* isomers (282.4 *vs.* 283.4 ppm for Mo and 257.1 *vs.* 256.1 ppm for W).

Although the π-back donation in the *mer* isomer being greater than in the *fac* isomer is deduced for both the bpy and dppe complexes, the phosphenium P–^{183}W coupling constants are greater for the bpy complexes than for the dppe complexes (IIIa *vs.* Va, IIIb *vs.* Vb, IIIc *vs.* Vc). The difference is 3.6 Hz between IIIa and Va, 22.6 Hz between IIIb and Vb, whereas the difference between IIIc and Vc is relatively large, 72.6 Hz. Therefore, it can be said that bpy ligand, especially when *trans* to the phosphenium ligand, can confer more stability on the phosphenium P–W bond than the dppe ligand can. In other words, bpy has weaker π-acidity than dppe, which is the same tendency as described by Chisholm *et al.* [7]. The same thing can be said for the Mo complexes. The greater stability for IIc than for IVc may be the reason for faster isomerization from IIb to IIc than from IVb to IVc.

A phosphenium ligand has been expected from molecular orbital calculations to serve as a strong π-acceptor on the model cation $[P(NR_2)_2]^+$ [8–11], and some static evidence has been shown; short M–P bonds have been revealed by X-ray analysis [2a,2c,3a], preference has been demonstrated of a phosphenium ligand for an equatorial position in trigonal-bipyramidal iron complexes [3b], and a higher frequency shift has been observed of ν(CO) in IR for the CO-containing phosphenium complexes [3b,4]. This work presents the first observation of dynamic behaviour of phosphenium complexes arising from its strong π-acceptability.

3. Experimental section

3.1. General remarks

All reactions were carried out under an atmosphere of dry nitrogen by Schlenk tube techniques. Hexane, xylene, toluene and THF were purified by distillation from sodium metal, and CH_2Cl_2 and CH_3CN were distilled from P_2O_5. They were stored under a nitrogen atmosphere. $BF_3 \cdot OEt_2$ was distilled prior to use.

IR spectra were recorded on a Shimadzu FTIR-4000 spectrometer. JEOL PMX-60, FX-100, and EX-400 spectrometers were used to obtain ^1H, ^{13}C, and ^{31}P NMR spectra. All chemical shifts are reported in ppm downfield from internal TMS (^1H and ^{13}C) and external 85% H_3PO_4 (^{31}P).

3.2. Starting materials

Literature methods were used for the preparation of $M(bpy)(CO)_4$ (M = Cr, Mo, W) [12], and $M(dppe)(CO)_4$ (M = Mo, W) [13]. $PN(Me)CH_2CH_2NMe(OMe)$ and complex IIa were synthesized according to literature methods [14,5b].

3.3. Synthesis of Ia

To a solution of $[Cr(bpy)(CO)_4]$ (2.12 g, 6.61 mmol) in toluene (100 ml) was added $PN(Me)CH_2CH_2NMe(OMe)$ (1.45 ml, 1.45 g, 9.92 mmol). After being refluxed for 1 h, the solution was allowed to cool in a refrigerator overnight. The resulting dark green crystals were isolated by filtration, washed with hexane, and dried *in vacuo* to give Ia (2.69 g, 6.11 mmol, 92%). Found: C, 48.86; H, 4.70; N, 12.41. $C_{18}H_{21}CrN_4O_4P$ calc.: C, 49.10; H, 4.81; N, 12.72%.

3.4. Synthesis of IIIa

To a solution of $[W(bpy)(CO)_4]$ (1.01 g, 2.21 mmol) in xylene (40 ml) was added $PN(Me)CH_2CH_2NMe(OMe)$ (0.49 ml, 0.49 g, 3.32 mmol). After being refluxed for 9 h, the solution was allowed to stand for several hours at room temperature. The resulting reddish purple precipitates were isolated by filtration, washed with hexane, and dried *in vacuo* to give IIIa (0.77 g, 1.35 mmol, 61%). The product was further purified for elemental analysis by column chromatography. The complex was loaded on an alumina column and eluted with THF. The first eluted purple band was collected. After concentration of the effluent under reduced pressure, hexane was added to give the crystalline IIIa, which was isolated by filtration, washed with hexane, and dried *in vacuo*. Found: C, 37.82; H, 3.78; N, 9.68. $C_{18}H_{21}N_4O_4PW$ calc.: C, 37.78; H, 3.70; N, 9.79%.

3.5. Synthesis of IVa

[Mo(dppe)(CO)$_4$] (2.00 g, 3.30 mmol) was put in a Pyrex tube, and CH_2Cl_2 (15 ml) and CH_3CN (250 ml) were added. The solution was irradiated with a 400 W medium pressure mercury arc lamp at 0°C for 5 h to give [Mo(dppe)(CO)$_3$(NCMe)] quantitatively (IR: ν(CO) = 1931, 1837, 1817 cm^{-1} in the solution). After removal of the solvents, THF (140 ml) and $\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}$ (0.63 ml, 0.63 mg, 4.29 mmol) were added. The solution was refluxed for 2.5 h and was allowed to cool to room temperature. The solution was concentrated to 40 ml under reduced pressure, and hexane (100 ml) was added to give pale yellow precipitates which were isolated by filtration, washed with hexane, and dried *in vacuo* to give IVa (1.80 g, 2.48 mmol, 76%). Found: C, 56.66; H, 5.18; N, 3.84. $C_{34}H_{37}MoN_2O_4P_3$ calc.: C, 56.21; H, 5.13; N, 3.85%.

3.6. Synthesis of Va

The complex Va was prepared in a similar manner to that of IVa from [W(dppe)(CO)$_3$(NCMe)] (IR: ν(CO) = 1924, 1828, and 1815 cm^{-1}) and $\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me(OMe)}$. Pale yellow crystals (yield 75%). Found: C, 50.26; H, 4.63; N, 3.25. $C_{34}H_{37}N_2O_4P_3W$ calc.: C, 50.14; H, 4.58; N, 3.44%.

3.7. Reaction of the phosphite complexes (Ia–Va) with $BF_3 \cdot OEt_2$

A solution of the phosphite complex (Ia–Va) (*ca.* 0.6 mmol) in CH_2Cl_2 (10 ml) was cooled to −78°C and 2 equiv. of $BF_3 \cdot OEt_2$ was added. The solution was then allowed to warm to room temperature. The resulting solution was subjected to the IR, ^{31}P NMR and, in some cases, ^{13}C NMR measurements. Ib: ^{31}P NMR δ (ppm) 263.8 (s). IIb: IR ν(CO) 2016, 1930, 1872 cm^{-1}; ^{31}P NMR δ (ppm) 252.5 (s). IIIb: IR ν(CO) 2006, 1920, 1868 cm^{-1}; ^{31}P NMR δ (ppm) 233.7 (J(PW) = 441.7 Hz). IVb: ^{31}P NMR δ (ppm) 282.4 (t, J(PP) = 29.0 Hz), 52.3 (d, J(PP) = 29.0 Hz). Vb: ^{31}P NMR δ (ppm) 257.1 (t, J(PP) = 22.1 Hz) (J(PW) = 41.9 Hz), 38.5 (d, J(PP) = 22.1 Hz) (J(PW) = 228.0 Hz). Ic: ^{31}P NMR δ (ppm) 277.3 (s). IIc: IR ν(CO) 1960, 1869, 1819 cm^{-1}; ^{31}P NMR δ (ppm) 268.2 (s). IIIc: IR ν(CO) 1952, 1860, 1813 cm^{-1}; ^{31}P NMR δ (ppm) 242.6 (s) (J(PW) = 561.1 Hz). IVc: ^{31}P NMR δ (ppm) 283.4 (dd, J(PP) = 119.0 and 27.5 Hz), 55.9 (dd, J(PP) = 27.5 and 12.2 Hz), 53.0 (dd, J(PP) = 119.0 and 12.2 Hz). Vc: ^{31}P NMR δ (ppm) 256.1 (dd, J(PP) = 114.0 and 19.0 Hz) (J(PW) = 488.5 Hz), 41.1 (d, J(PP) = 19.0 Hz) (J(PW) = 224.3 Hz), 36.8 (d, J(PP) = 114.0 Hz) (J(PW) = 235.1 Hz).

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