Retardation Effect of Trimethyl Phosphite on Chelate Ring Closure of 2,2′-Bipyridine (bipy) in *cis*-[W(CO)$_4${P(OMe)$_3$}-(bipy)]

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In order to study the effect of a donor ligand on the chelate ring-closure reaction of a diimine ligand co-ordinated in monodentate fashion, *cis*-[W(CO)$_4${P(OMe)$_3$}(bipy)] was synthesised from [W(CO)$_5${P(OMe)$_3$}] and 2,2′-bipyridine (bipy) by using a newly developed method and characterized by means of IR and NMR spectroscopies. The complex was found to undergo neither *cis* ⟶ *trans* isomerization nor chelation thermally up to 150 °C. However the ring-closure reaction occurs photochemically. Thus irradiation of the complex yielded *fac*-[W(CO)$_3${P(OMe)$_3$}(bipy)] which was also isolated and characterized. The extraordinary retardation effect of trimethyl phosphite on the ring-closure reaction of the 2,2′-bipyridine ligand is attributed to the reduction in substitution lability of the CO groups in the complex upon introduction of the phosphite donor ligand.

In binding to the transition metals, diimines (L–L) can act either as mono-[1–4] or bi-dentate ligands.[4–7] In the latter case they form stable tetracarbonyldiiminemetal(0) complexes with the Group 6 elements, thermally or photochemically.[8–13] In the photolysis of [M(CO)$_6$] with L–L the formation of chelate complexes has been thought to occur subsequent to the photochemical generation of [M(CO)$_5$(L–L)] species, in which L–L is co-ordinated in a monodentate fashion [equations (1) and (2)].

$$[\mathrm{M(CO)_6}] + \text{L–L} \xrightarrow{h\nu} [\mathrm{M(CO)_5(L–L)}] + \mathrm{CO} \quad (1)$$

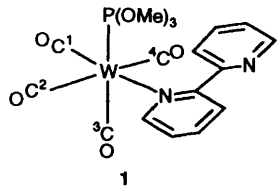
$$[\mathrm{M(CO)_5(L–L)}] \xrightarrow{\text{heat}} [\mathrm{M(CO)_4(L–L)}] + \mathrm{CO} \quad (2)$$

Despite extensive studies of the overall photochemical substitution reaction and the structure of the final product, relatively little is known about the nature of the intermediates which have been photogenerated in solution.[14] Spectroscopic evidence has been reported for the formation of [M(CO)$_5$(L–L)] during photolysis of [M(CO)$_6$] in the presence of diimines which have a strong inclination for chelation.[15–18] Although [M(CO)$_5$(L–L)] is thought to be generated in solution, it undergoes rapid chelate ring closure to form stable [M(CO)$_4$(L–L)] even at low temperatures in the case of diimines having high preference for chelation, such as 2,2′-bipyridine (bipy) or 2,7-dimethyl-3,6-diazaocta-3,5-diene (diazabutadiene, dab). The use of pentacarbonyl(η^2-olefin)metal(0) as a M(CO)$_5$ transfer reagent[19] provides a convenient way to isolate [M(CO)$_5$(dab)] as the olefin ligand can be substituted by dab even at low temperatures.[20] The [M(CO)$_5$(dab)] complexes were shown to be stable at temperatures below zero and to undergo chelate ring-closure reactions at higher temperature, the kinetics of which was studied in the case of chromium.[21] However, the use of M(CO)$_5$ as transfer reagent does not liberate [M(CO)$_5$(bipy)]; instead, one obtains exclusively [M(CO)$_4$(bipy)] even at low temperatures. This implies that bipy has a much stronger propensity for chelation than does dab, which is attributed to electronic and steric factors.[10]

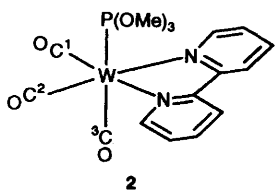
It is not unexpected that the rate of chelation of the diimine ligand would also be affected by the presence of ligands other than carbonyl. It is known that the presence of a donor ligand can affect the metal–ligand bonding sterically as well as electronically.[22] Therefore, we thought that introducing a donor ligand into the [M(CO)$_5$(L–L)] complex would slow down the chelation, so that the kinetics of the ring-closure reaction could be studied at moderate temperatures. Indeed, metal carbonyl complexes containing both a donor ligand (L) and a diimine ligand are known.[5,6,23–26] However, in all the known complexes, the diimine is co-ordinated in a bidentate manner. It must undergo rapid chelation in the synthesis, and [M(CO)$_3$L(L–L)] is formed. Therefore, in order to isolate [M(CO)$_4$L(L–L)] in which L–L is co-ordinated in a monodentate fashion, one has to find a preparation method in which its chelation is retarded under the reaction conditions. The irradiation of [M(CO)$_5$L] in the presence of L–L was thought to be suitable. Indeed, photolysis of [W(CO)$_5$L] with bipy was found to generate *cis*-[W(CO)$_4$L(bipy)] **1**, which is however converted into *fac*-[W(CO)$_3$L(bipy)] **2** during irradiation, where L = P(OMe)$_3$ [equation (3)]. The formation of **1** and **2** exclusively as the *cis* and *fac* isomer, respectively, can be attributed to the fact that the W–CO bond *trans* to the P(OMe)$_3$ ligand is considerably strengthened by the latter which has less π-acceptor, but greater σ-donor character than does carbon monoxide. Owing to the photosubstitution of a second CO group by the free end of the bipy ligand, the amount of **1** in the irradiated solution is never sufficient for isolation. Instead, one obtains **2** as the only isolated product of the photolysis. The irradiation was interrupted when **1** is spectroscopically observable in order to see whether there is any change in the concentration of **1** in the dark, but none was observed at room temperature. From this observation, one can conclude that **1** is thermodynamically stable, but undergoes chelate ring closure photochemically to form **2**. To isolate **1** one therefore has to find a preparation method which is applicable in the dark. The use of a W(CO)$_4$L transfer reagent is thought to be ideal for co-ordination of bipy in a monodentate fashion.

$$[\mathrm{W(CO)_5L}] + \text{bipy} \xrightarrow[-\mathrm{CO}]{h\nu} [\mathrm{W(CO)_4L(bipy)}] \xrightarrow[-\mathrm{CO}]{h\nu} fac\text{-}[\mathrm{W(CO)_3L(bipy)}] \quad (3)$$

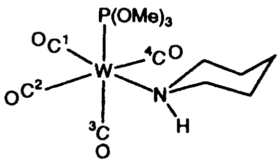
Here, we report a method developed for the synthesis of complex **1** which is the first example of a metal carbonyl complex containing a donor ligand and a diimine ligand which has a strong tendency for chelation. The method is based on a sequence of simple substitution reactions starting from pentacarbonyl(trimethyl phosphite)tungsten(0)[27] [equations



1



2



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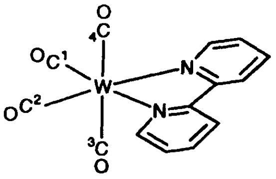

4

(4) and (5); thf = tetrahydrofuran, r.t. = room temperature].

$$[W(CO)_5\{P(OMe)_3\}] + thf \xrightarrow[r.t.]{h\nu} [W(CO)_4\{P(OMe)_3\}(thf)] + CO \quad (4)$$

$$[W(CO)_4\{P(OMe)_3\}(thf)] + bipy \xrightarrow{heat} [W(CO)_4\{P(OMe)_3\}(bipy)] + thf \quad (5)$$

For the purpose of comparison and interpretation of spectroscopic data, *cis*-$[W(CO)_4\{P(OMe)_3\}(pip)]$ **3** (pip = piperidine) was synthesised in the same way; $[W(CO)_4(bipy)]$ **4** was also prepared, according to the procedure described in the literature,[28] to record its ^{13}C NMR data. Longer irradiation of $[W(CO)_5\{P(OMe)_3\}]$ in the presence of bipy results in the formation of *fac*-$[W(CO)_3\{P(OMe)_3\}(bipy)]$ **2**. All the complexes were isolated and purified by recrystallization, and characterized by IR, ^1H, ^{31}P and ^{13}C NMR spectroscopic methods.

Experimental

All of the reactions and manipulations were carried out either *in vacuo* or under a dry deoxygenated nitrogen atmosphere. Solvents were distilled after refluxing over metallic sodium or phosphorus pentaoxide under nitrogen for 3–4 d and stored until used. Hexacarbonyltungsten(0), 2,2′-bipyridine, trimethyl phosphite and piperidine were obtained from Aldrich Chemical Co. and used without further purification. The photochemical reactions and other treatment of organometallic compounds such as purification and crystallization were monitored by IR spectroscopy at appropriate time intervals.

The NMR spectra were recorded on a Bruker AC-80 spectrometer (80.131 MHz for ^1H, 32.442 MHz for ^{31}P and 20.149 MHz for ^{13}C). Phosphoric acid (85%) in a capillary tube was used as external reference for ^{31}P NMR, $SiMe_4$ as internal reference for ^1H and ^{13}C NMR. Infrared spectra were recorded from solution on a Perkin-Elmer 1430 instrument. Elemental analyses were carried out on an Hewlett-Packard 185 CHN analyzer. Photochemical reactions were carried out in an irradiation apparatus by using a Hanau TQ 150 high-pressure mercury lamp. The complexes $[W(CO)_4(bipy)]$ and $[W(CO)_5\{P(OMe)_3\}]$ were prepared as described.[28,29]

(2,2′-Bipyridine)tetracarbonyl(trimethyl phosphite)tungsten(0), *cis*-$[W(CO)_4\{P(OMe)_3\}(bipy)]$ **1**.—A solution of $[W(CO)_5\{P(OMe)_3\}]$ (0.5 g, 1.4 mmol) in thf (100 cm^3) was irradiated for 1 h at room temperature. To the dark orange solution of *cis*-$[W(CO)_4\{P(OMe)_3\}(thf)]$ was added bipy (2.2 g, 1.4 mmol) and the mixture stirred for 3 h. As the exchange reaction proceeded the solution turned from dark orange to red. The solvent was removed completely under vacuum. The red residue containing $[W(CO)_4\{P(OMe)_3\}(bipy)]$ was washed with cold hexane several times in order to remove unreacted starting materials. Yield 0.3 g (40%) (Found: C, 34.90; H, 2.90; N, 2.30. Calc. for $C_{17}H_{17}N_2O_4PW$: C, 35.35; H, 2.95; N, 2.40%). NMR: ^{31}P (see Table 1); ^1H ($CDCl_3$), δ 8.66, 8.45 (H^3); 8.25, 8.12 (H^4); 7.71, 7.30 (H^5); 9.27, 8.72 (H^6) (the second resonance of each pair is assigned to the unco-ordinated ring of the bipy ligand); 3.33 $[P(OMe)_3]$; ^{13}C (see Table 2). IR: ν(CO) 2008w, 1917w, 1894s and 1827m cm^{-1}.

Table 1 The ^{31}P NMR chemical shifts (δ, relative to H_3PO_4), co-ordination shifts (Δδ, relative to free phosphite) and $^{183}W-^{31}P$ coupling constants (Hz) of the complexes in $[^2H_8]$toluene

Complex	δ	Δδ	$J(^{183}W-^{31}P)$
1	146.25	5.25	380
2	146.41	5.41	380
3	145.40	4.40	382

(2,2′-Bipyridine)tricarbonyl(trimethyl phosphite)tungsten(0), *fac*-$[W(CO)_3\{P(OMe)_3\}(bipy)]$ **2**.—A solution of $[W(CO)_5\{P(OMe)_3\}]$ (0.5 g, 1.4 mmol) and bipy (3.0 g) in toluene (100 cm^3) was irradiated for 3 h at room temperature. Removal of solvent left a dark violet residue. Crystallization from toluene yielded dark violet crystals of *fac*-$[W(CO)_3\{P(OMe)_3\}(bipy)]$. Yield 0.3 g (43%) (Found: C, 38.10; H, 3.30; N, 5.35. Calc. for $C_{16}H_{17}N_2O_7PW$: C, 38.40; H, 3.45; N, 5.60%). NMR: ^{31}P (see Table 1); ^1H ($CDCl_3$), δ 7.32 (H^3), 7.91 (H^4), 8.15 (H^5), 9.39 (H^6); 3.36 $[P(OMe)_3]$; ^{13}C (see Table 2). IR: ν(CO) 1923w, 1887s and 1798m cm^{-1}.

Tetracarbonyl(piperidine)(trimethyl phosphite)tungsten(0), *cis*-$[W(CO)_4\{P(OMe)_3\}(pip)]$ **3**.—A solution of $[W(CO)_5\{P(OMe)_3\}]$ (0.5 g, 1.4 mmol) in thf (100 cm^3) was irradiated for 1 h at room temperature. An excess of piperidine (2 cm^3) was added to the dark orange solution of *cis*-$[W(CO)_4\{P(OMe)_3\}(thf)]$. As the exchange reaction proceeded, the solution turned from dark orange to golden yellow. The solvent was removed completely under vacuum. The yellow residue containing *cis*-$[W(CO)_4\{P(OMe)_3\}(pip)]$ was washed with cold hexane several times in order to remove unreacted starting materials. Yield 0.4 g (70%) (Found: C, 27.90; H, 2.75; N, 2.75. Calc. for $C_{12}H_{19}NO_4PW$: C, 28.30; H, 2.80; N, 2.80%). NMR: ^{31}P (see Table 1); ^1H ($CDCl_3$), δ 2.71 (H^1), 3.82 (H^2), 3.72 (H^3), 2.61 (H^4); 3.12 $[P(OMe)_3]$; ^{13}C (see Table 2). IR: ν(CO) 2018w, 1911w, 1889s and 1861m cm^{-1}.

Results and Discussion

The IR spectra of complexes **1** and **3** show four strong absorption bands in the CO stretching region indicating a *cis* arrangement of the $W(CO)_4$ moiety.[30] Complex **2** gives three strong CO-stretching bands indicating that it has a facial arrangement of the $W(CO)_3$ moiety.[30]

The $^{31}P-\{^1H\}$ NMR spectra of complexes **1**–**3** show only one signal for $P(OMe)_3$ accompanied by tungsten satellites (Table 1). This indicates the existence of one isomeric form. The signal of the trimethyl phosphite ligand appears at a lower magnetic field compared to that of free $P(OMe)_3$.[27] The co-ordination shift in **1** and **2** is slightly larger than that in **3**, reflecting higher electron donation from phosphorus to the metal due to the π-accepting ability of the bipyridine ligand.

The ^{13}C NMR spectra of complexes **1** and **3** show three doublets, due to $^{31}P-^{13}C$ coupling, with relative intensities 2:1:1 for the carbonyl groups (Table 2). This indicates a *cis* arrangement of the four CO groups, consistent with the IR results. The signal of the relative intensity 2 is readily assigned to the CO groups *trans* to each other, but *cis* to both of the nitrogen- and phosphorus-containing ligands. Complex **1** shows

Table 2 The ^{13}C NMR chemical shifts (δ, relative to $SiMe_4$) and ^{13}C–^{31}P coupling constants (Hz, in parentheses) of the complexes in $CDCl_3$; u = unco-ordinated part of bipy

	bipy	**1**	**2**	**3**	**4**
CO 1		221.11 (9.6)	222.48 (9.1)	206.68 (7.8)	215.67
CO 2		206.15 (39)	222.48 (9.1)	202.88 (11)	215.67
CO 3		205.63 (32)	211.71 (64)	207.47 (53)	202.45
CO 4		206.15 (39)		202.88 (11)	202.45
C^2	156.45	156.81 156.70 (u)	155.67	58.41 (2.7)	156.63
C^3	137.12	139.19 137.55 (u)	135.79	27.48	139.19
C^4	124.04	127.52 126.50 (u)	126.08	22.50	127.48
C^5	121.13	124.50 123.84 (u)	122.53		124.46
C^6	149.47	153.55 153.00 (u)	152.38		153.48
$P(OMe)_3$		51.34 (3.7)	51.22 (3.7)	51.89 (3.7)	

a large ^{31}P–^{13}C coupling constant for these CO groups which can be attributed to the π-accepting property of the bipy ligand. When co-ordinated in monodentate fashion, bipy is a single-faced ligand similar to a carbene.[31] Since the π orbital of bipy will interact with only one metal d orbital, d_{xz} or d_{yz} (z being the W–N direction), one of these two d orbitals will be less involved in the π interaction between tungsten and phosphorus or carbonyl (CO 2 and CO 4). This will result in localization of the W–P and W–CO π interactions in the plane (xy) perpendicular to the W–N bond. The reinforcement of the W–P and W–C bonds in the xy plane will certainly enlarge the corresponding ^{31}P–^{13}C coupling constant. One of the other two doublets with relative intensities 1 : 1 has a large ^{31}P–^{13}C coupling constant and therefore might be assigned to the CO group *trans* to the trimethyl phosphite ligand.[32]

It is useful to compare the chemical shifts of CO *trans* to the N-containing ligand in complexes **1** and **3**. A remarkable downfield shift is observed for **1**. This is attributed to the single-faced π-acceptor character of the bipy ligand, similar to that of a carbene which also causes a large downfield shift of a *trans*-carbonyl signal.[33] A lowfield shift is observed for the carbonyls *trans* to nitrogen atoms in **4**, as well as in **2** (Table 2).

The ^{13}C NMR spectrum of complex **1** shows ten signals for the bipy ligand indicating that the two aromatic rings are different. By considering the presence of the $W(CO)_4$ unit, one can readily conclude that bipyridine is co-ordinated in a monodentate fashion. The observation of only five signals for the diimine ligand in **2** indicates bidentate co-ordination of bipyridine. Comparison of the chemical shifts for one- or two-side co-ordinated bipyridine in **1** and **2** with those of free bipyridine as well as with those of the same ligand in **4** enables us to make an unequivocal assignment of the ^{13}C NMR signals. Thus it is seen that the introduction of the donor ligand in **1** and **2** does not cause any noticeable change. This may be explained by the single-faced character of bipy. The W–N π interaction is not very sensitive to the ligands in the plane perpendicular to the W–N axis as discussed earlier.

The ^{13}C NMR spectrum of piperidine gives three signals for three different carbon atoms (Table 2). The signal which appears as doublet due to ^{31}P–^{13}C coupling is assigned to carbons 2 and 6 which are deshielded upon co-ordination to the transition metal (free piperidine: δ 47.7, 27.5 and 26.1[34]). This clearly implies an electron drift from piperidine to the metal centre.

As expected, the presence of trimethyl phosphite stabilizes the complex containing bipy as monodentate ligand. Complex **1** is stable even in solution up to 150 °C. It undergoes neither *cis* ⟶ *trans* isomerization nor chelate ring closure in the dark. Remembering the extreme instability of (2,2′-bipyridine)-pentacarbonyltungsten(0),[10] the large stabilization effect of trimethyl phosphite is a fascinating result. However, **1** undergoes ring closure photochemically to form **2**. The fact that chelation occurs photochemically but not thermally (up to 150 °C) may imply that the activation energy of the ring-closure reaction is increased by introducing trimethyl phosphite into the complex. Both electronic and steric factors may be responsible for this effect. Ring closure may be prevented by the strong σ-donor interaction of the trimethyl phosphite which strengthens the remaining W–CO bonds. Alternatively, or in addition, the reaction may be slowed by the bulkiness of the trimethyl phosphite which hampers such an associative thermal, but not the dissociative photochemical, chelate ring-closure reaction.

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