Metal Carbonyl Complexes Involving 2,6-Bis[1-(phenylimino)ethyl]pyridine; Bidentate Coordination of a Potentially Tridentate Ligand

JOHN M. ALBON, DENNIS A. EDWARDS* and PHILIP J. MOORE
School of Chemistry, University of Bath, Bath BA2 7AY, U.K.

(Received August 26, 1988)

Abstract

The isolation and spectrosocopic characterisation of six complexes, *cis*-[M(CO)$_4$L^2] (M = Mo, W), *fac*-[Mo(CO)$_3$(NCMe)L^2], *fac*-[M'Br(CO)$_3$L^2] (M = Mn, Re) and *fac*-[Re(CO)$_3$(NCMe)L^2]ClO$_4$, are reported with L^2 = the Schiff base ligand 2,6-bis[1-(phenylimino)ethyl]pyridine. This ligand, which has previously been shown to act as a planar tridentate in a wide range of complexes, behaves as a bidentate chelating ligand in all the above complexes bonding through the pyridyl nitrogen and one imine nitrogen only.

Introduction

Lu and Selbin recently reported [1] that the potentially tridentate ligand L^1 (R = (CH$_3$)$_3$CCH$_2$) reacts with Mo(CO)$_6$ to give only *cis*-[Mo(CO)$_4$L^1], a single crystal X-ray structure determination showing that L^1 is acting as a bidentate chelating ligand bonding through the pyridyl nitrogen and only one of the imino nitrogen donor atoms. We report here the results of a number of related reactions involving some Groups VI and VII metal carbonyls and the Schiff base L^2 (R = C$_6$H$_5$) (Fig. 1). Spectroscopic evidence indicates that in all the products L^2 is similarly bidentate rather than tridentate, so this may prove to be a common feature of reactions between octahedral metal carbonyls or their derivatives and ligands of this type. However, it is well established that L^2 behaves in the expected manner as a planar tridentate ligand in its reactions with various nickel(II), copper(II), zinc(II) and cadmium(II) halides, nitrates and perchlorates [2–8], the products being either five- or six-coordinate complexes. So although many reactions of L^2 with metal salts have been reported, we are not aware of any previous reports of reactions of L^2 with metal carbonyls.

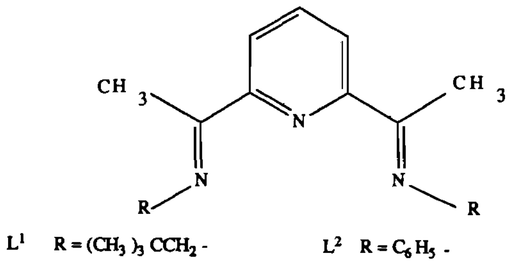

Fig. 1. Structural formulae.

Experimental

Starting Materials

2,6-Bis[1-(phenylimino)ethyl]pyridine was prepared from freshly distilled aniline and 2,6-diacetylpyridine in refluxing ethanol–glacial acetic acid (50:1) as previously described [2]. It was recrystallised from ethanol before use. Yield, 89%; melting point 158 °C. *Anal.* Calc. for C$_{21}$H$_{19}$N$_3$: C, 80.5; H, 6.11; N, 13.4. Found: C, 80.5; H, 6.09; N, 13.4%.

Molybdenum and tungsten hexacarbonyls were used as received and MnBr(CO)$_5$ [9], ReBr(CO)$_5$ [10] and [Re(CO)$_3$(NCMe)$_3$]ClO$_4$ [11] prepared by literature procedures.

Physical Measurements

Solution and mull infrared spectra were recorded using a Perkin-Elmer 599B spectrometer. Conductivity measurements were carried out at 25 °C on 10^{-3} M solutions using a Wayne-Kerr Autobalance bridge and a dip-type cell with platinum electrodes. Proton NMR spectra were recorded using Jeol PS 100 and GX 270 spectrometers. Carbon, hydrogen and nitrogen microanalyses were performed by Butterworth Laboratories or at the University of Bath by Mr A. Carver.

Reaction Procedures

All reactions were carried out in an atmosphere of dry nitrogen and all solvents were dried and deoxygenated by purging with nitrogen before use.

cis-[Mo(CO)$_4$L^2]

(i) Molybdenum hexacarbonyl (0.34 g, 1.29 mmol) and L^2 (0.40 g, 1.28 mmol) were reacted in

---

*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

refluxing 2,2-dimethoxypropane (35 cm^3) for 1 h. Removal of the solvent *in vacuo* left a dark maroon solid that was purified by chromatography using a column of Brockmann grade 1 neutral alumina and dichloromethane as eluant. Removal of dichloromethane *in vacuo* gave a dark red, somewhat air-sensitive, solid. Yield, 0.28 g (42%). *Anal.* Calc. for $C_{25}H_{19}MoN_3O_4$: C, 57.6; H, 3.64; N, 8.05. Found: C, 57.8; H, 3.69; N, 8.13%.

(ii) The above reaction can also be successfully performed in refluxing sodium-dried toluene for 90 min giving a 73% yield of the desired product.

fac-[$Mo(CO)_3(NCMe)L^2$]

A solution of *fac*-[$Mo(CO)_3(NCMe)_3$] was prepared, using a literature procedure [12], from $Mo(CO)_6$ (1.00 g, 3.23 mmol) in refluxing acetonitrile (20 cm^3). The completion of the reaction was monitored by infrared spectroscopy. After cooling of the bright yellow solution, solid L^2 (1.20 g, 3.84 mmol) was added, and the solution briefly refluxed again. On cooling in ice, a deep violet, air-sensitive, solid crystallised and was collected by filtration and dried *in vacuo*. Yield, 0.64 g (37%). *Anal.* Calc. for $C_{26}H_{22}MoN_4O_3$: C, 58.4; H, 4.12; N, 10.5. Found: C, 58.1; H, 4.52; N, 10.7%.

cis-[$W(CO)_4L^2$]

A solution of *cis*-[$W(CO)_4(NCMe)_2$] was prepared by reacting $W(CO)_6$ (1.00 g, 2.84 mmol) in refluxing acetonitrile (30 cm^3) for 64 h. Infrared monitoring of this slow reaction indicated the presence of only trace amounts of [$W(CO)_5(NCMe)$] and *fac*-[$W(CO)_3(NCMe)_3$] after this reaction time. After cooling, solid L^2 (0.89 g, 2.84 mmol) was added to the yellow solution and on refluxing for a further 30 min a deep red solution resulted. Cooling in ice gave a dark red crystalline product which was collected by filtration and dried *in vacuo*. Further product could be obtained by concentration of the filtrate and addition of diethyl ether. Yield, 0.85 g (49%). *Anal.* Calc. for $C_{25}H_{19}N_3O_4W$: C, 49.3; H, 3.12; N, 6.90. Found: C, 49.0; H, 3.18; N, 7.07%.

fac-[$MnBr(CO)_3L^2$]

A reaction between $MnBr(CO)_5$ (0.20 g, 0.73 mmol) and L^2 (0.25 g, 0.80 mmol) was carried out in refluxing 2,2-dimethoxypropane (25 cm^3) for 5 min. The resulting orange crystals were filtered, washed with further 2,2-dimethoxypropane and recrystallised from dichloromethane–petroleum spirit. Yield, 0.365 g (94%). *Anal.* Calc. for $C_{24}H_{19}BrMnN_3O_3$: C, 54.1; H, 3.57; N, 7.89. Found: C, 53.9; H, 3.57; N, 7.60%.

fac-[$ReBr(CO)_3L^2$]

A reaction between $ReBr(CO)_5$ (0.20 g, 0.49 mmol) and L^2 (0.16 g, 0.51 mmol) in refluxing 2,2-dimethoxypropane (20 cm^3) for 90 min gave golden orange crystals on cooling. The product was recrystallised from acetonitrile–diethyl ether. Yield, 0.31 g (96%). *Anal.* Calc. for $C_{24}H_{19}BrN_3O_3Re$: C, 43.4; H, 2.87; N, 6.33. Found: C, 42.4; H, 2.90; N, 6.13%.

fac-[$Re(CO)_3(NCMe)L^2$]ClO_4

The complex *fac*-[$Re(CO)_3(NCMe)_3$]ClO_4 (0.20 g, 0.41 mmol) was treated with L^2 (0.14 g, 0.45 mmol) in refluxing chloroform (30 cm^3) for 48 h. Infrared monitoring revealed that no reaction had taken place. The reaction was repeated in refluxing tetrahydrofuran (30 cm^3) for 6 h. Removal of the solvent *in vacuo* left a solid residue that was redissolved in acetonitrile (5 cm^3). The solution was filtered and diethyl ether added to the filtrate to give a yellow solid that was collected by filtration and dried *in vacuo*. Yield: 0.26 g (87%). *Anal.* Calc. for $C_{26}H_{22}ClN_4O_7Re$: C, 43.1; H, 3.04; N, 7.74. Found: C, 43.8; H, 3.05; N, 7.46%.

Results and Discussion

The ligand properties of 2,6-bis[1-(phenylimino)ethyl]pyridine, L^2, (alternatively named 2,6-diacetylpyridinebis(anil)), have been investigated by Alyea and co-workers [2–8] who isolated and characterised a variety of products. In all of the resulting complexes e.g. five-coordinate [MX_2L^2] (M = Ni, Zn or Cd; X = halide) and six-coordinate [ML^2_2]X_2 (M = Ni, Zn, X = ClO_4; M = Ni, Cu, Zn or Cd, X = NO_3; M = Ni, X = Br, I, BF_4 or $\frac{1}{2}Ni(CN)_4$), [$M(\eta^2\text{-}NO_3)XL^2$] (M = Ni, Zn or Cd; X = Cl, Br), [$M(\eta^2\text{-}NO_3)(\eta^1\text{-}NO_3)L^2$] (M = Ni, Cu, Zn or Cd) and [$M(\eta^1\text{-}NO_3)(en)L^2$]$^+$ (M = Ni, Zn), the ligand L^2 is invariably tridentate as would be expected of this planar NNN-donor containing one pyridyl group and two equivalent phenylimino moieties. Single-crystal X-ray structure determinations of octahedral [$M(\eta^2\text{-}NO_3)(\eta^1\text{-}NO_3)L^2$] (M = Ni [3] and Cu [5]) and of trigonal bipyramidal [$ZnCl_2L^2$]·1.5MeCN and [$MnBr_2L^2$]·C_6H_6 [13] show that L^2 spans three in-plane bonding positions. Acting as a tridentate ligand, only the three meridional positions of an octahedron can be occupied by the donor nitrogen atoms of L^2, the enforced planarity of the donor atoms prohibiting the alternative facial array. In this respect L^2 behaves like the best known terdentate nitrogen donor ligand, 2,2′:6′,2″-terpyridine.

However, a recent report of the preparation and structure determination [1] of *cis*-[$Mo(CO)_4L^1$] suggests that this class of ligand may also display bidentate behaviour with one imino-nitrogen not coordinated to a metal. Again a relationship with 2,2′:6′,2″-terpyridine, which forms *cis*-[$M(CO)_4(\eta^2\text{-}terpy)$] (M = Cr, Mo or W) complexes [14], is apparent and a few other Schiff bases behave similarly, e.g. *E*-pyridine-2-carbaldehyde 2′-pyridylhydrazone which forms *cis*-[Mo(CO)$_4$(η^2-*E*-paphy)] rather than *mer*-[Mo(CO)$_3$(η^3-*E*-paphy)] [15]. We report here the isolation and spectroscopic characterisation (Table 1) of six complexes involving L^2 bonded as a bidentate, rather than tridentate, ligand.

The reaction of Mo(CO)$_6$ with L^2 in refluxing 2,2-dimethoxypropane or toluene affords *cis*-[Mo(CO)$_4$L^2]. The dichloromethane solution infrared spectrum of the product shows four bands in the ν(CO) region, typical of a *cis*-[Mo(CO)$_4$XY] species, at very similar frequencies to those of *cis*-[Mo(CO)$_4$L^1], *cis*-[Mo(CO)$_4$(η^2-terpy)] [14] and, indeed, *cis*-[Mo(CO)$_4$(bipy)] [16]. No evidence could be found for the formation of *mer*-[Mo(CO)$_3$L^2] in which L^2 would be tridentate. The difficulty of replacing a further carbonyl ligand from *cis*-[Mo(CO)$_4$(NN-donor)] type complexes to produce *mer*-[Mo(CO)$_3$(NN-donor)X] species is well established, the easy route to a *fac*-isomer not being available to L^2. This effect has been explained by consideration of carbonyl ligand π-bonding effects, a carbonyl *trans* to another carbonyl being more labile than a carbonyl *trans* to a donor nitrogen atom.

The possibility that [Mo(CO)$_4$L^2] contains tridentate L^2 would seem to be most unlikely because the metal would be seven-coordinate with 20 rather than 18 valence electrons. The proton NMR spectrum of this complex in CD$_2$Cl$_2$ provides evidence that L^2 is only bidentate. Two sharp methyl proton singlets of equal intensities, well separated by 0.38 ppm, are detected showing the inequivalence of the two C$_6$H$_5$N=C(CH$_3$) substituents on the pyridine ring. One singlet is unshifted relative to that of free L^2, the other being at lower field. As expected, only single methyl proton resonances are observed [2] for both ZnCl$_2$L^2 and [ZnL$_2{}^2$][ClO$_4$]$_2$ in which L^2 is terdentate, both at lower field than L^2 itself.

Similarly, the reaction of *cis*-[W(CO)$_4$(NCMe)$_2$] with L^2 gives *cis*-[W(CO)$_4$L^2] in which L^2 is again bidentate rather than tridentate, as confirmed by spectroscopic evidence (Table 1). The shift of the methyl singlet assigned to that of the coordinated side-chain, relative to free L^2, is somewhat greater (0.44 ppm) than that of the molybdenum analogue. This tungsten complex could not be prepared from W(CO)$_6$ and L^2 in refluxing toluene, no significant amount of product being formed after 72 h.

One other Group VI metal carbonyl derivative containing bidentate L^2 has been isolated, namely *fac*-[Mo(CO)$_3$(NCMe)L^2]. This complex was prepared by displacement of only two of the three usually easily replaceable acetonitrile ligands of *fac*-[Mo(CO)$_3$(NCMe)$_3$]. No rearrangement to *mer*-[Mo(CO)$_3$(η^3-L^2)] was detected. The three strong band pattern in the ν(CO) region of the solution infrared spectrum is that expected for an octahedral metal tricarbonyl complex of local C_s symmetry in which the three different donor nitrogen atoms, pyridyl, imino and nitrile, are coordinated facially. The methyl resonances observed in the proton NMR spectrum in CD$_2$Cl$_2$ solution confirm this proposed structure. Three sharp singlets of equal intensity are detected, those at 2.44 and 2.80 ppm being assigned to uncoordinated and coordinated C$_6$H$_5$N=C(CH$_3$) moieties of bidentate L^2 and that at 2.00 ppm to coordinated acetonitrile, slightly downfield of the free acetonitrile resonance position in CD$_2$Cl$_2$, (1.95 ppm).

TABLE 1. Spectroscopic Data for L^2 and its Complexes

Compound	Proton NMR, δ (ppm) CH$_3$ resonances (CD$_2$Cl$_2$ solution)	IR ν(CO) bands
L^2	2.40 (s, 6H)	
cis-[Mo(CO)$_4$L^2]	2.40 (s, 3H) uncoord. 2.78 (s, 3H) coord.	2005(s), 1910(s) 1880(s), 1840(s)^a
fac-[Mo(CO)$_3$(NCMe)L^2]	2.00 (s, 3H) C*H*$_3$CN 2.44 (s, 3H) uncoord. 2.80 (s, 3H) coord.	1905(s), 1810(s), 1795(s)^b
cis-[W(CO)$_4$L^2]	2.40 (s, 3H) uncoord. 2.84 (s, 3H) coord.	2004(s), 1985(s) 1885(s), 1839(s)^c
fac-[MnBr(CO)$_3$L^2]	2.42 (s, 3H) uncoord. 2.56 (s, 3H) coord.	2031(s), 1945(s), 1924(s)^c
fac-[ReBr(CO)$_3$L^2]	2.44 (s, 3H) uncoord. 2.49 (s, 3H) coord.^{d}	2018(s), 1926(s), 1900(s)^c
fac-[Re(CO)$_3$(NCMe)L^2]ClO$_4$	2.00 (s, 3H) C*H*$_3$CN 2.48 (s, 3H) uncoord. 2.80 (s, 3H) coord.	2028(s), 1925(s, br)

^{a}CH$_2$Cl$_2$ solution. ^{b}CH$_3$CN solution. ^{c}CHCl$_3$ solution. ^{d}CD$_3$CN solution.

Three Group VII metal carbonyl derivatives containing bidentate L^2 have also been isolated and spectroscopically characterised. Reactions of $MBr(CO)_5$ (M = Mn, Re) with L^2 in refluxing 2,2-dimethoxypropane give high yields of *fac*-$[MBr(CO)_3L^2]$ after recrystallisation. The chloroform solution infrared spectra of these two complexes in the ν(CO) region consist of three bands all of similar strong intensities. This pattern is in agreement with a facial stereochemistry with a pyridyl nitrogen, an imino nitrogen and the bromine *trans* to three mutually *cis* carbonyl groups. A *mer* isomer is unlikely to be formed because in the $MBr(CO)_5$ species the carbonyl *trans* to bromine is more strongly bonded to the metal and so is less easily replaced than the other four carbonyl groups [17]. The actual ν(CO) frequencies are closely similar to those of related *fac*-$[MBr(CO)_3(bipy)]$ complexes (M = Mn, 2029, 1932, 1921 cm^{-1}; M = Re, 2025, 1925, 1898 cm^{-1}). The presence of bidentate L^2 allows an eighteen valence electron count for the metals and the presence of tridentate L^2 can be excluded by a consideration of proton NMR and conductance data. The observation of two methyl proton singlets in the NMR spectra of both complexes (Table 1) is again indicative of the presence of coordinated and uncoordinated $C_6H_5N=C(CH_3)$ substituents on the pyridine ring of L^2. An alternative eighteen electron formulation would be ionic $[M(CO)_3(\eta^3\text{-}L^2)]Br$. Not only is this structure ruled out by the above NMR data but it has also been shown that both complexes are non-electrolytes as 10^{-3} M solutions at 25 °C in dichloromethane, (M = Mn, $\Lambda_M = 0.32$ ohm^{-1} cm^2 mol^{-1}; M = Re, Λ_M = 0.24 ohm^{-1} cm^2 mol^{-1}; *cf.* $[Mn(CO)_3(NCMe)_3]ClO_4$, Λ_M = 23.6 ohm^{-1} cm^2 mol^{-1}). It is therefore concluded that the $[MBr(CO)_3L^2]$ complexes are *fac*-octahedral involving bidentate L^2. The Group VI complexes, discussed above, are also, as expected, non-electrolytes in dichloromethane.

Finally, reaction of *fac*-$[Re(CO)_3(NCMe)_3]ClO_4$ with L^2 in refluxing tetrahydrofuran followed by recrystallisation from acetonitrile gives a good yield of *fac*-$[Re(CO)_3(NCMe)L^2]ClO_4$ with no evidence of the formation of *mer*-$[Re(CO)_3(\eta^3\text{-}L^2)]ClO_4$. The product is a 1:1 electrolyte in dichloromethane (Λ_M = 22.7 ohm^{-1} cm^2 mol^{-1} for a 10^{-3} M solution at 25 °C) and the proton NMR spectrum in CD_2Cl_2 is very similar to that of *fac*-$[Mo(CO)_3(NCMe)L^2]$, three methyl singlets of equal intensities being observed in agreement with the presence of one acetonitrile ligand and a bidentate L^2 ligand. A mull infrared spectrum confirms the presence of both ionic perchlorate (strong bands at 1096 ν(ClO) and 625 δ(OClO) cm^{-1}) and coordinated acetonitrile (weak bands at 2282 ν(CN) and 2306 $\delta_{sym}(CH_3) + \nu_{sym}$(CC) cm^{-1}). However, the chloroform solution infrared spectrum in the ν(CO) region consists of only two strong bands (Table 1) rather than the three predicted on symmetry arguments. The lower frequency band is, however, broad and this type of ν(CO) band pattern has been observed previously [11] for several related *fac*-$[Re(CO)_3(NCMe)(L\text{-}L)]^+$ cations (L-L = e.g. bipy, dipyam). It seems that the lower frequency ν(CO) band is only split into a well-resolved doublet when the π-acceptor abilities of the L-L ligands are markedly different (e.g. phosphines, arsines) to those of acetonitrile.

References

1 S. Lu and J. Selbin, *Inorg. Chim. Acta, 134* (1987) 229.
2 E. C. Alyea and P. H. Merrell, *Syn. React. Inorg. Met.-Org. Chem., 4* (1974) 535.
3 E. C. Alyea, G. Ferguson and R. J. Restivo, *Inorg. Chem., 14* (1975) 2491.
4 E. C. Alyea, G. Ferguson, R. J. Restivo and P. H. Merrell, *J. Chem. Soc., Chem. Commun.*, (1975) 269.
5 R. J. Restivo and G. Ferguson, *J. Chem. Soc., Dalton Trans.*, (1976) 518.
6 E. C. Alyea and P. H. Merrell, *Inorg. Chim. Acta, 28* (1978) 91.
7 P. H. Merrell, E. C. Alyea and L. Ecott, *Inorg. Chim. Acta, 59* (1982) 25.
8 E. C. Alyea, *Inorg. Chim. Acta, 76* (1983) L239.
9 R. B. King, *Organomet. Synth., 1* (1965) 174.
10 S. P. Schmidt, W. C. Trogler and F. Basolo, *Inorg. Synth., 23* (1985) 44.
11 D. A. Edwards and J. Marshalsea, *J. Organomet. Chem., 131* (1977) 73.
12 D. P. Tate, W. R. Knipple and J. M. Augl, *Inorg. Chem., 1* (1962) 433.
13 D. A. Edwards, P. E. Fanwick, M. F. Mahon, W. R. Martin, K. C. Molloy and R. A. Walton, unpublished observations.
14 M. C. Ganorkar and M. H. B. Stiddard, *J. Chem. Soc.*, (1965) 5346.
15 J. G. Dunn and D. A. Edwards, *J. Chem. Soc. A*, (1971) 988.
16 M. H. B. Stiddard, *J. Chem. Soc.*, (1962) 4712.
17 R. J. Angelici, F. Basolo and A. J. Poë, *J. Am. Chem. Soc., 85* (1963) 2215.