Journal of Organometallic Chemistry, 331 (1987) 23–28
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Substituted metal carbonyls

III *. Chromium, molybdenum and tungsten tricarbonyl complexes containing bipyridyl and a unidentate diphosphine: facile synthesis via trimethylamine *N*-oxide-induced decarbonylations

T.S. Andy Hor ** and Sheh-Mai Chee

Department of Chemistry, Faculty of Science, National University of Singapore, Kent Ridge 0511 (Singapore)

(Received February 16th, 1987)

Abstract

The ability of trimethylamine *N*-oxide as a chemical initiator for facile oxidative decarbonylation in metal carbonyls is manifested by the isolation of $M(CO)_3(\eta^2\text{-bipy})(\eta^1\text{-dppm})$ (where M = Cr, Mo, W; bipy = 2,2′-bipyridyl; dppm = bis(diphenylphosphino)-methane). The synthetic strategy and spectral (IR and ^1H and ^{31}P NMR) characterisations are presented and discussed. Syntheses of the well-known $M(CO)_4(\eta^2\text{-bipy})$ have also been modified to give high yields at ambient temperature.

Introduction

α-Diimine ligands [3–5] as exemplified by 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy) serve as a very important class of ligands in metal carbonyl chemistry. Especially distinctive are the kinetically labile and fluxional di- and tri-substituted Group VIA metal carbonyls [6]. Explication of kinetic and mechanistic details in these systems plays a crucial role in understanding their substitution [7–9] and isomerisation [10] processes. Most of such investigations [11–15] however are confined to carbonyl displacement by a monodentate ligand, viz.

$$M(CO)_4(bipy) + L \rightarrow M(CO)_3(bipy)(L) + CO$$

(M = Cr, Mo and W; L = 2-electron donor)

---

* For parts 1 and 2 see refs. 1 and 2.

** To whom correspondence should be addressed.

0022-328X/87/$03.50

Bidentate ligands (LL′) are rarely used in such studies because of the possible complication of displacing the bipy ligand to yield M(CO)$_4$(LL′). Hence up to now, there has been a lack of a convenient and systematic method for making mixed-ligand derivatives of neutral metal tricarbonyls [16,17], particularly those which contain two different bifunctional ligands. The present report offers a facile 2-step synthesis of M(CO)$_3$(η^2-bipy)(η^1-dppm) * (M = Cr, Mo and W) starting from the metal hexacarbonyls by using trimethylamine *N*-oxide (TMNO) as the initiator. The phen analogue of these compounds has been reported recently [2].

Results and discussion

Preparations of the well-documented Cr(CO)$_4$(η^2-bipy), Mo(CO)$_4$(η^2-bipy) and W(CO)$_4$(η^2-bipy) [18–23] have been modified to give good yields (81, 85 and 97% respectively). Oxidative decarbonylation of M(CO)$_6$ with TMNO in the presence of the ligand in bezene or benzene/methanol mixture proceeds readily at room temperature to give the highly-coloured tetracarbonyls. Conventional thermolytic and photochemical techniques [18,24–26] which are arduous and non-selective have been avoided.

The second step involves a stoichiometrically controlled replacement of a carbonyl by a unidentate dppm ligand. Similarly, the substitution is facilely induced by TMNO at room temperature. The tricarbonyl complexes, M(CO)$_3$(η^2-bipy)(η^1-dppm) (M = Cr, **1**, Mo, **2**, and W, **3**) have been characterised (see Table 1) spectroscopically (IR, ^{1}H and ^{31}P NMR).

Table 1

Spectroscopic data

Complex (M.p. (°C))	ν(CO) (cm^{-1})	δ(^{1}H) (ppm)	δ(^{31}P) (ppm)
Cr(CO)$_3$(bipy)(dppm) **1** (153, dec)	1909s, 1824m, 1785m	9.42(br) [d,H^6(bipy)], 7.02–8.25 [m,C$_6$H$_5$ and H^{3,4,5}-(bipy)], 2.77(br) [d, CH$_2$-(dppm)]	*fac*-; 45.77(d,1P), −27.06 (d,1P); *J*(PP) 49 Hz *mer*-; 29.55 (d, 1P), −27.87(d,1P), *J*(PP) 51 Hz [a]
Mo(CO)$_3$(bipy)(dppm) **2** (212, dec)	1915s, 1821m, 1789m	8.84 [d,H^6(bipy)], 6.73–7.83 [m,C$_6$H$_5$ and H^{3,4,5}-(bipy)], 2.63 [dd,CH$_2$-(dppm)]; *J*(HP$_a$) 5.0 Hz, *J*(HP$_b$) 2.3 Hz	27.26 (d,1P), −27.93 (d,1P); *J*(PP) 73 Hz [b]
W(CO)$_3$(bipy)(dppm) **3** (120, dec)	1908s, 1816m, 1784m	8.93 [d,H^6(bipy)], 6.73–8.46 [m,C$_6$H$_5$ and H^{3,4,5}-(bipy)], 2.70 [dd,CH$_2$-(dppm)]; *J*(HP$_a$) 5.7 Hz, *J*(HP$_b$) 2.0 Hz	20.33 (d,1P), −27.12 (d,1P); *J*(PP) 64 Hz [a]

[a] CDCl$_3$. [b] DMAC (*N*,*N*-dimethylacetamide).

---

* dppm = bis(diphenylphosphino)methane.

Complexes **1** and **3** are novel but **2** has been briefly mentioned in the literature [27]. The latter complex, prepared from $Mo(CO)_3(C_7H_8)$ (where $C_7H_8 =$ cycloheptatriene) via the carbonyl-bridged dimer $(\mu_2\text{-}CO)_2Mo_2(CO)_4(\eta^2\text{-bipy})_2$ [28,29] however, lacks firm spectroscopic support. The chromium analogue of the dimer was hitherto unknown.

It is generally accepted that TMNO is effective in promoting decarbonylation at ambient temperature for metal carbonyls with IR $\nu(CO) > 2000\ cm^{-1}$ [30–32]. This conception is in accord with the present conversion of tetracarbonyl to tricarbonyl complexes as all the former species exhibit an IR band a little above 2000 cm^{-1}. For complexes **1**, **2** and **3**, despite the proximity of the uncoordinated phosphorus to the metal centre and the expected stability for a M–P–C–P–M four-membered chelate, cyclisation of the dppm ligand and formation of the higher substituted dicarbonyl derivatives has not been detected at room temperature even with an excess of TMNO. Such inertness for chelation however is not unexpected in view of the low $\nu(CO)$ for all the three tricarbonyls (the highest absorptions occur 85–92 cm^{-1} below 2000 cm^{-1}).

Formation of **1**, **2** and **3** from their tetracarbonyl counterparts can be easily seen in changes in their IR spectra. A common pattern of three strong absorptions $(a_1 + 2e)$ suggests a *fac*-configuration for the $M(CO)_3$ moiety [2,21,33–36], which is understood in view of the *cis*-labilising effect of the bipy ligand [37–39].

The ^1H NMR spectra suggest that the usual resonances are assignable to η^2-bipy ligation [7]. The doublets of a doublet, ^1H–^{31}P coupling, for the methylene protons of dppm implies the chemical inequivalence of the two phosphorus nuclei. Unambiguous evidence for the unidentate coordination mode of the phosphine is deduced from the ^{31}P NMR analysis. The presence of two mutually coupled non-equivalent phosphorus NMR resonances together with the occurrence of a high field signal of similar chemical shifts (Table 1) relative to free dppm molecule (δ −21.67 ppm) [1,2] typify all three spectra. Tungsten satellites were not observed in the spectrum of **3** owing to the limited solubility of the complex in the NMR solvent. The downfield resonance due to the ligated phosphorus demonstrates a decrease in coordination shift, defined as $\delta_{complex} - \delta_{free\ ligand}$, [40–42] in the expected order of Cr (67.44 ppm) > Mo (48.93 ppm) > W (42.00 ppm). Similar trends of comparable magnitudes were observed for the analogous phen complexes [2]. Among the three complexes studied, only **1** shows a minor quantity of its *mer*-isomer in the ^{31}P NMR spectrum.

It is envisaged that the title compounds cannot be satisfactorily prepared via the classical thermolytic or photolytic pathway from $M(CO)_6$. Competitive substitutions would lead to the formation of more familiar complexes such as $M(CO)_4(\eta^2\text{-dppm})$ [43], $M(CO)_2(\eta^2\text{-dppm})_2$ [44] or $M(CO)_3(\eta^2\text{-dppm})\ (\eta^1\text{-dppm})$ [45,46]. Attempts to prepare the related complexes $M(CO)_3(\eta^2 - \text{dppm})(\eta^1\text{-dipy})$ have so far proved unsuccessful. This is however not too surprising considering the negligible *cis*-labilising ability of the phosphine [47] and the unstable coordinating mode for a unidentate bipy.

All the above-mentioned octahedral carbonyls which contain mixed ligands either in chelating or dangling form are potentially important models for kinetic and mechanistic studies in metal carbonyl reactions [48,49]. Their good π-accepting ability, coupled with the anionic behaviour of ligands such as bipy and phen, would enable these complexes to be useful for electrochemical experiments [50,51]. Redox chemistry, in particular, is expected to be rich [52]. The versatile coordination ability of these ligands is manifested by their potential as syphons for heterometallic mixed-ligand derivatives of dinuclear and polynuclear metal carbonyls [53].

Conclusion

Tricarbonyl Group VIA metal complexes containing a bidentate bipy and a unidentate dppm ligand have been synthesised from a chemically-induced decarbonylation pathway under mild conditions. This strategy is particularly useful for thermally unstable or UV sensitive compounds and for those which contain kinetically labile ligands. Our success with the bipy, phen and dppm groups have prompted extension of our work to include other α-diimines and diphosphines. Investigations on the generalisation of this methodology and the reactivities of these substituted carbonyls are currently in progress.

Experimental

General procedure

All reactions were performed under pure dry dinitrogen using standard Schlenk techniques. Solvents were of reagent grade and degassed before use. Proton NMR spectra were recorded on a JEOL FX 90Q at 89.55 MHz using $(CH_3)_4Si$ as internal standard and $CDCl_3$ as solvent. Phosphorus-31 NMR spectra were recorded in $CDCl_3$ or DMAC on the same spectrometer at 36.23 MHz. Chemical shifts are reported in ppm to high frequency of external 85% phosphoric acid. Infrared spectra were run as chloroform solutions on a FT-IR Perkin–Elmer 1710 IR spectrometer. Melting points were measured using a Thomas Hoover Unimelt capillary melting point apparatus without calibration. Elemental analyses were performed by the Analytical Service of this department. All the instruments mentioned above were available in this department. Spectroscopic (NMR and IR) data are given in Table 1 together with the melting points. Dppm was purchased from Aldrich Chemical Co. and was checked for purity by ^{13}C and ^{31}P NMR spectroscopy before use. Metal hexacarbonyls, bipy and TMNO (dihydrate) were purchased from Aldrich, Merck and Tokyo Kasei Kogyo Co. Ltd. respectively and were used without further purification.

Reactions

$W(CO)_4(\eta^2$-bipy). A solution of TMNO (0.3396 g, 3.06 mmol) in methanol (5 ml) was added to a vigorously-stirred solution of $W(CO)_6$ (0.5032 g, 1.43 mmol) in benzene. To this yellow mixture was added bipy (0.2351 g, 1.51 mmol) which immediately gave a red suspension. After stirring for 18 h at 28° C, the mixture was reduced to low volume and filtered. The maroon microcrystals thus isolated were analytically pure; they can, however, be recrystallised from CH_2Cl_2/hexane. Yield: 0.63 g (97%). IR $\nu(CO)$: 2008m, 1900vs, 1880sh 1829s [18]. Found: C, 37.19; H, 1.64; N, 6.19. $C_{14}H_8N_2O_4W$ calc: C, 37.17; H, 1.77; N, 6.19%.

$M(CO)_4(\eta^2$-dipy) (M = Cr, Mo). A similar procedure was adopted as for the W analogue except that neat benzene was used in the Cr complex. The products were analytically pure and their IR spectra checked against literature values [18]. Yields: 0.62 g (81%, based on 0.5050 g of $Cr(CO)_6$) and 0.62 g (85%, based on 0.5271 g of $Mo(CO)_6$).

$Mo(CO)_3(\eta^2$-bipy)(η^1-dppm). A mixture of $Mo(CO)_4(\eta^2$-bipy) (0.1655 g, 0.45 mmol), TMNO (0.0719 g, 0.64 mmol) and dppm (0.1782 g, 0.46 mmol) in CH_3CN (25 ml) was stirred to give a clear violet solution. Evaporation to dryness in vacuo yielded a purple solid which was redissolved in CH_2Cl_2 and filtered. To the filtered solution was added methanol, followed by evaporation to low volume under vacuum. The purple precipitate thus formed was isolated by filtration. A second crop of product was usually obtained from the filtrate upon addition of methanol followed by slow evaporation. The combined crop was recrystallised from $CHCl_3/CH_3OH$. Yield: 0.18 g (54%). Found: C, 63.72; H, 3.86; N, 3.56. $C_{38}H_{30}MoN_2O_3P_2$ calc: C, 63.33; H, 4.10; N, 3.83%.

$Cr(CO)_3(\eta^2$-bipy)(η^1-dppm). A mixture of $Cr(CO)_4(\eta^2$-bipy) (0.2961 g, 0.93 mmol), TMNO (0.1156 g, 1.04 mmol) and dppm (0.4102 g, 1.07 mmol) in CH_3CN (30 ml) was stirred for 17 h to give a maroon suspension. A purple solid was isolated after filtration and a second crop was obtained by reducing the volume of the filtrate, which was subsequently cooled to −20 °C and filtered. Repeated recrystallisations from CH_2Cl_2/hexane gave the analytically pure product. Yield: 0.27 g (40%). Found: C, 67.15; H, 4.81; N, 4.33. $C_{38}H_{30}CrN_2O_3P_2$ calc: C, 67.46; H, 4.44; N, 4.14%.

$W(CO)_3(\eta^2$-bipy)(η^1dppm). A similar procedure was adopted as for the Cr analogue. Purple microcrystals (yield 0.13 g (40%)) were obtained from $W(CO)_4(\eta^2$-bipy) (0.1810 g, 0.40 mmol), TMNO (0.2303 g, 2.08 mmol) and dppm (0.3496 g, 0.91 mmol). Found: C, 56.25; H, 3.86; N, 2.99. $C_{38}H_{30}N_2O_3P_2W$ calc: C, 56.42; H, 3.72; N, 3.47%.

Acknowledgement

The authors express their gratitude to the National University of Singapore for financial support (Grant No. RP850030) and Mr. Chong Thiam Cheong for experimental assistance.

References

1 T.S.A. Hor, J. Organomet. Chem., 319 (1987) 213.
2 T.S.A. Hor, Inorg. Chim. Acta., 128 (1987) L3.
3 R.A. Howie and G.P. McQuillan, J. Chem. Soc., Dalton Trans., (1986) 759.
4 B.J. Brisdon, D.W. Brown, C.R. Willis and M.G.B. Drew, J. Chem. Soc., Dalton Trans., (1986) 2405.
5 D.M. Manuta and A.J. Lees, Inorg. Chem., (1986) 1354.
6 G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 3, Ch. 26–28, Pergamon Press, Oxford, 1982.
7 J.A. Connor, E.J. James, C. Overton, J.M.A. Walshe and R.A. Head, J. Chem. Soc., Dalton Trans., (1986) 511.
8 M. Basato, J. Chem. Soc., Dalton Trans., (1986) 217.
9 H. Elias, H.-T. Macholdt, K.J. Wannowius, M.J. Blandamer, J. Burgess and B. Clark, Inorg. Chem., (1986) 3048.
10 G.R. Dobson, H.H. Awad and S.S. Basson, Inorg. Chim. Acta, 118 (1986) L5.
11 R.W. Balk, T. Snoeck, D.J. Stufkens and A. Oskam, Inorg. Chem., 19 (1980) 3015.
12 W.H. de Roode, D.G. Prins, A. Oskam and K. Vrieze, J. Organomet. Chem., 154 (1978) 273.
13 M. Dokiya, R.D. Johnston and F. Basolo, Inorg. Chem., 9 (1970) 996.
14 G.R. Dobson and K.J. Asali, J. Am. Chem. Soc., 101 (1979) 5433.
15 M.A. Cohen and T.L. Brown, Inorg. Chem., 15 (1976) 1417.
16 L.W. Houk and G.R. Dobson, J. Chem. Soc., (1966) 317.

17 G.P. McQuillan and S.E. Pritchard. Inorg. Chim. Acta, 53 (1981) L141.
18 M.H.B. Stiddard, J. Chem. Soc. (A), (1962) 4712.
19 H.D. Murdoch, R. Henzi and F. Calderazzo, J. Organomet. Chem., 7 (1967) 441.
20 J.R. Graham and R.J. Angelici. Inorg. Chem., 6 (1967) 992.
21 G.R. Dobson and L.W. Houk, Inorg. Chim. Acta, 1 (1967) 287.
22 H. Saito, J. Fujita and K. Saito, Bull. Chem. Soc. Jap., 41 (1968) 359.
23 B. Hutchinson and K. Nakamoto, Inorg. Chim. Acta, 3 (1969) 591.
24 M.H.B. Stiddard, J. Chem. Soc., (1963) 756.
25 E.W. Abel, M.A. Bennett and G. Wilkinson, J. Chem. Soc., (1959) 2323.
26 H. Behrens and D. Herrmann, Z. Anorg. Allg. Chem., 357 (1967) 225.
27 H. Behrens. W. Topf and J. Ellermann. J. Organomet. Chem., 63 (1973) 349.
28 H. Behrens, E. Lindner and G. Lehnert, J. Organomet. Chem., 22 (1970) 439.
29 H. Behrens, G. Lehnert and H. Sauerborn, Z. Anorg. Allg. Chem., 374 (1970) 310.
30 M.O. Albers and N.J. Coville. Coord. Chem. Rev., 53 (1984) 227 and references therein.
31 T.Y. Luh, Coord. Chem. Rev., 60 (1984) 255 and references therein.
32 U. Koelle, J. Organomet. Chem., 133 (1977) 53.
33 D.M. Adams in Edward Arnold (Ed.), Metal-Ligand and Related Vibrations, London, 1967, p. 101.
34 F.A. Cotton, Inorg. Chem., 3 (1964) 702.
35 J.M. Jenkins, J.R. Moss and B.L. Shaw, J. Chem. Soc. (A), (1969) 2796.
36 J. Dalton, I. Paul, J.G. Smith and F.G.A. Stone, J. Chem. Soc. (A), (1968) 1208.
37 R.J. Angelici and J.R. Graham, J. Am. Chem. Soc., 87 (1965) 5586.
38 J.R. Graham and R.J. Angelici, J. Am. Chem. Soc., 87 (1965) 5590.
39 J.D. Atwood and T.L. Brown, J. Am. Chem. Soc., 98 (1976) 3160.
40 J.F. Nixon and A. Pidcock, Ann. Rev. NMR Spectroscopy, 2 (1969) 345.
41 B.E. Mann, C. Masters, B.L. Shaw, R.M. Slade and R.E. Stainbank, Inorg. Nucl. Chem. Letters, 7 (1971) 881.
42 J.A. Connor, J.P. Day, E.M. Jones and G.K. McEwen, J. Chem. Soc., Dalton Trans., (1973) 347.
43 K.K. Cheung, T.F. Lai and K.S. Mok, J. Chem. Soc. (A), 10 (1971) 1644
44 A.M. Bond, R. Colton and J.J. Jackowski, Inorg. Chem., 14 (1975) 2526.
45 E.E. Isaacs and W.A.G. Graham. Inorg. Chem., 14 (1975) 2560.
46 A. Blagg, A.T. Hutton, B.L. Shaw, M. Thornton-Pett, Inorg. Chim. Acta, 100 (1985) L33.
47 R.J. Angelici, Organomet. Chem. Rev., 3 (1968) 173.
48 J.A. Connor and G.A. Hudson. J. Organomet. Chem., 73 (1974) 351.
49 D.J. Darensbourg, Adv. Organomet. Chem., 21 (1982) 113.
50 A.M. Bond, S.W. Carr, R. Colton and D.P. Kelly, Inorg. Chem., 22 (1983) 989.
51 A. Blagg, S.W. Carr, G.R. Cooper, I.D. Dobson, J.B. Gill, B.L. Shaw, D.C. Goodall, N. Taylor and T. Boddington, J. Chem. Soc., Dalton Trans., 6 (1985) 1213.
52 A. Blagg, G.R. Cooper, P.G. Pringle, R. Robson and B.L. Shaw, J. Chem. Soc., Chem. Commun., 14 (1984) 933.
53 S.W. Carr, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Dalton Trans., (1985) 2131 and references therein.