Journal of Organometallic Chemistry, 366 (1989) 121–127
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09731

Bis(pyrazolyl)methanetetracarbonyl-chromium(0), -molybdenum(0) and -tungsten(0)

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(Received October 5th, 1988)

Abstract

Bis(pyrazolyl)methanetetracarbonyl-chromium(0), -molybdenum(0) and -tungsten(0) were prepared from $M(CO)_6$ and characterized by IR, ^1H and ^{13}C NMR spectroscopy. They are of only moderate stability as solid or in solution, being more stable in acetone than in DMSO. They are less stable than other compounds containing a chelating nitrogen ligand attached to a $M(CO)_4$ group, and the reasons for this are discussed.

Introduction

Poly(azol-1-yl)alkanes, $(Az)_nCH_{4-n}$, (AzH = di-, tri- or tetra-azole; $n = 2$, 3, or 4) from an interesting family of polydentate nitrogen ligands, which are extensively used, especially when the azole is pyrazole [1]. In the case of bis- or tris-pyrazolylalkanes, derivatives of several elements are known, e.g.: zinc(II) and cadmium(II) [2a], mercury(II) and mercury(I) [2b], tin(IV) [2c] and organotin(IV) [2d], rhodium(I) [2f,e], iridium(I) [2f], platinum(II) [2g] and platinum(IV) [2h], palladium(II) [2g], copper(I) [2i] or copper(II) [2j], silver(I) [2k], or gold [2l]. Nevertheless, neither carbonyl nor zerovalent metal derivatives of this family of ligands had been reported, and so we decided to try to prepare them. Our reasons for this are that (a) carbonylmetal derivatives of a ligand afford an easy, though indirect way of evaluating some of its donor properties, (b) comparison can be made with carbonyl derivatives of other polydentate ligands, and, (c) a substantial amount of photochemical work has been carried out with the related $M(CO)_4$(bipyridyl) derivatives (M = group VI metal) [3].

Results and discussion

From various attempts, only three compounds (L–L)$M(CO)_4$ (L–L = bis(pyrazolyl)methane; M = Cr, Mo or W; **1**, **2** or **3**, respectively) could be isolated.

0022-328X/89/$03.50

Table 1

Some physical data for the compounds prepared

Compound	Yield (%)	Elemental analyses (Found (calcd.) (%))			Specific conductivity [a] (ohm^{-1} cm^2 mol^{-1})
		C	H	N	
(L–L)Cr(CO)$_4$ (1)	57	42.46 (42.32)	2.77 (2.58)	17.66 (17.95)	(1.00) 6.12
(L–L)Mo(CO)$_4$ (2)	52	37.25 (37.10)	2.57 (2.26)	15.62 (15.73)	(1.01) 1.08
(L–L)W(CO)$_4$ (3)	43	29.90 (29.75)	1.98 (1.82)	12.86 (12.62)	(1.03) 3.32

[a] Acetone solution at room temperature and at the molar concentration $\times 10^{-3}$ indicated in parentheses.

These were made by the following reactions, carried out under nitrogen in an aromatic hydrocarbon and in the presence of an excess of ligand:

$$M(CO)_6 + L\text{–}L \rightarrow (L\text{–}L)M(CO)_4 + 2\ CO$$

$$(M = Mo,\ W)$$

$$Cr(CO)_6 + L\text{–}L + 2\ Me_3NO \rightarrow (L\text{–}L)Cr(CO)_4 + 2\ Me_3N + 2\ CO_2$$

The first reaction did not take place with chromium. Both reactions took place with bis(pyrazolyl)methane. No product could be isolated when the ligand was bis(3,5-dimethylpyrazol-1-yl)methane, bis(4-nitropyrazol-1-yl)methane, 2,2′-bis(pyrazol-1-yl)propane, tris(pyrazol-1-yl)methane, or bis(1,2,4-triazol-1-yl)methane, and the metal-containing substrate was either hexacarbonylmolybdenum, (norbornadiene)tetracarbonylmolybdenum, or, in the case of Pz_3CH, (cycloheptatriene)(tricarbonyl)molybdenum.

The compounds obtained (Table 1) are greenish-yellow (Mo, W) or green (Cr) solids, with stabilities falling in the order Mo > W ≫ Cr; the chromium complex cannot be kept in the air for long, a hydrated species being formed. They are non-electrolytes in acetone, in which the most stable of them reacts immediately with 1,2-bis(diphenylphosphinoethane), L–L being displaced and $(CO)_4Mo(Ph_2PCH_2)_2$ (4) isolated.

The infrared spectra showed the bands corresponding to both the carbonyl and the heterocyclic ligands. In the carbonyl stretching region, four bands were expected for the *cis*-arrangement of the ligands and were found in the Nujol spectra. The solution spectra are limited to these in acetonitrile or acetone (Table 2) for solubility reasons, but the spectra of compounds **1**–**3** are comparable with those of other (L′–L′)M(CO)$_4$ compounds where L′–L′ is *N*,*N*,*N*′,*N*′-tetramethylethylendiammine, 2,2′-bipyridyl, phenanthroline (or its 1,9-dimethyl derivative) or two mol of pyridine (Table 2).

The proton and carbon-13 NMR data, recorded for all the compounds in acetone and in dimethylsulphoxide solvent are listed in Table 3 and Table 4, respectively. All the signals due to the organic ligands could be detected, but only one ^{13}C carbonyl signal was observed, although two were expected: either these molecules are fluxional, or, more likely, one signal was undetected owing to the limited solubility, which also prevented observation of coupling with ^{95}Mo or ^{183}W.

Table 2

Infrared carbonyl stretching frequencies (cm^{-1})

Compound	Solvent	Bands
(L–L)$Cr(CO)_4$ (**1**)	Nujol [a]	2010s, 1900sh, 1880s, 1810s
(L–L)$Mo(CO)_4$ (**2**)	Nujol	2010s, 1910sh, 1870s, 1810s
	Acetone [b]	2010vs
	Acetonitrile	2015s, 1900vs, 1855s
$(py)_2Mo(CO)_4$	THF [c]	2015, 1889, 1860
$(bpy)Mo(CO)_4$	THF [c]	2039, 1938, 1900, 1838
$(tmeda)Mo(CO)_4$	THF [c]	2038, 1878, 1836
$(Me_2phen)Mo(CO)_4$	THF [c]	2035, 1900, 1836
$(phen)Mo(CO)_4$	THF [c]	2041, 1900, 1884, 1844
$(Ph_2MeP)_2Mo(CO)_4$	THF [c]	2036, 1954, 1922, 1900
$(dppe)Mo(CO)_4$	THF [c]	2040, 1956, 1932, 1924, 1900
	CH_2Cl_2 [d]	2020s, 1919sh, 1907vs, 1881s
	CH_2Cl_2	2025s, 1905sh, 1900s, 1870s
(L–L)$W(CO)_4$ (**3**)	Nujol	2005s, 1905sh, 1865s, 1805s
	Acetone [b]	2020m
	Acetonitrile	2020s, 1915vs, 1890s

[a] This compound decomposes in acetone and acetonitrile. [b] Obscured by solvent at < ca. 1900 cm^{-1}. [c] From ref. 4a. [d] From ref. 4b.

In acetone solution both the Mo and W compounds are stable, and only one set of signals is observed, as expected. However, an additional set is present for the chromium compound, characterized by the absence of any additional carbonyl and by the presence of signals which are, approximately in the positions of the signals of the ligand. It seems, then, that in the chromium derivative the solvent molecules

Table 3

^1H NMR data

Compound	Solvent	Values [a] for CH_2 and pyrazole ring		
		CH_2	4-CH	3- or 5-CH [b]
L–L	DMSO-d_6	6.39s	6.28t (1.8)	7.93d (2.1)
				7.49d (1.4)
	$(CD_3)_2CO$	6.45s	6.39t (1.8)	7.98d (1.8)
				7.61d (1.5)
	$CDCl_3$	6.30s	6.26t (1.2)	7.63d (2.4)
				7.55d (1.8)
1 [c]	$(CD_3)_2CO$	6.65s	6.42t (1.4)	8.15d (2.0)
				8.00d (1.4)
		6.50s	6.28t (1.2)	7.88d (2.2)
				7.46d (1.2)
2	$(CD_3)_2CO$	6.77s	6.48t (2.0)	8.22d (1.8)
				8.00d (1.6)
3	$(CD_3)_2CO$	6.80s ′	6.48t (1.6)	8.22d (1.8)
				8.10d (1.4)

[a] δ in ppm from internal TMS: s, singlet, d, doublet, t, triple; in parentheses J in Hz. [b] The signal with higher J value belongs to C(3), the other to C(5) in accord with ref. 2e. [c] The intensity ratio between the set in the upper line (compound) and the set in the lower line (ligand) is ca. 3/1.

Table 4

^{13}C NMR data [a]

Compound	Solvent	C(3)	C(4)	C(5)	CH_2	CO
L–L	DMSO-d_6	140.1	106.3	130.5	65.4	
	$(CD_3)_2CO$	140.2	106.4	130.1	65.1	
	$CDCl_3$	140.6	107.0	129.5	65.1	
1	$(CD_3)_2CO$ [b]	140.0	106.8	130.5	65.3	–
		146.9	107.7	134.1	62.9	206.4
2	DMSO-d_6 [b]	140.0	106.4	130.5	64.2	–
		146.2	107.2	133.9	62.6	220.4
	$(CD_3)_2CO$	146.9	107.7	133.9	63.7	211.0
3	DMSO-d_6 [b]	140.0	106.2	130.5	64.2	–
		146.9	107.7	133.9	63.4	218.0
	$(CD_3)_2CO$	147.6	108.2	133.9	64.5	213.0

[a] Chemical shifts in ppm from internal TMS. No ^{95}Mo–C or ^{183}W–C coupling was observed. [b] The signals in the upper line are due to the ligand, those in the lower line to the complex. Relative intensity ligand/complex: compound **1** ca. 2/1, compound **2** ca. 1/3, compound **3** ca. 1/2.

displace the ligand L–L from the coordination sphere. The same conclusion applies to all the compounds when a stronger donor than acetone, namely DMSO, is used as the solvent (Table 4). If the relative intensities of the signals is assumed to be roughly proportional to the concentration of the species under observation, in DMSO the ratio of ligand to complex is ca. 2, 1/3 and 1/2 for the chromium, molybdenum, and tungsten complexes, respectively. In other words, in this solution the stability order is Mo > W ≫ Cr, as found for the stability upon storage in the solid state.

The ^{1}H NMR spectra (Table 3) also show that the chromium compound is the least stable of the three, two sets of signals being observed.

The molecular weight determination in acetone, provides independent confirmation that there is no dissociation in this solvent.

When the ^{13}C or ^{1}H NMR spectra of the coordinated and of the free ligand are compared, some general trends are apparent, namely: (i) in the proton spectra all the signals are displaced to lower field upon coordination; (ii) of all the proton signals, the least displaced is H(4); (iii) in the ^{13}C spectra only the pyrazole signals are displaced downfield, while the CH_2 signals are either unaffected or displaced slightly upfield. In acetone with our new compounds the difference D (the shift for the complex minus that for the ligand in the same solvent) varies from 1.3 to 7.6

Table 5

Molecular weight determinations [a]

Compound	Formula weight (FW)	Solvent	conc. (%, w/w)	MW	MW/FW
1	384.3	Acetone	0.96	unstable	
2	356.2	Acetone	1.20	367	1.03
3	444.1	Acetone	0.75	428	0.96

[a] By osmometry

ppm and from 0.2 to 1.4 ppm, respectively; similar observations apply to the DMSO solutions.

These or similar trends have been well documented with the group IIB derivative [2], the tin(IV) and organotin(IV) adducts [2c,d], as well as for a series of rhodium(I) and iridium(I) complexes [2e], so that, even in the absence of additional data, it is tempting to suggest that these empirical trends indicate a general validity. For *N*-substituted azoles some empirical rules do apply; e.g. both chemical shifts and coupling constants can be discussed in terms of simple additivity models [5]. Furthermore empirical rules concerning internal and external angles in the pyrazoles [6], as well as the various metal derivatives of pyrazoles [7], have been proposed.

The moderate stability of the (L–L)M(CO)$_4$ (**1**–**3**), as well as our failure to isolate similar products containing a bis- or a tris(pyrazolyl)alkane is, at first, surprising for three reasons: (i) many stable (L′–L′)M(CO)$_4$ compounds are known, such as those listed in Table 2; (ii) several adducts between metal or organometal cations and bis- or tris(pyrazolyl)alkenes have been isolated, such as those referred to in the introduction; and (iii) there is the possibility of some back donation from the zerovalent metal to a π^* orbital of the pseudoaromatic ligand, as in pyridine (which gives stable Py$_2$M(CO)$_4$ complexes). In connection with the last point, back donation, if any, is more difficult with pyrazole than with pyridine, since only the former is an electron-rich pseudoaromatic. As for reason (i), some very recent thermochemical data [4a] on the stability of several (ligand)$_2$Mo(CO)$_4$ compounds have shown that the complex containing 1,10-phenanthroline is some 5 kcal/mole more stable than the corresponding 2,2′-bipyridine derivative: displacement of bound bipyridine will allow relaxation to the preferred conformation of the free ligand, whereas no such energy gain is possible with phenanthroline, a rigid ligand. If such an interpretation is extended to our species, displacement of bound L–L from (L–L)M(CO)$_4$ will allow bis(pyrazolyl)methane to relax to the conformation with least energy; since this ligand is more flexible than bipyridine, its complexes will be even more unstable, as found. Finally, concerning reason (ii), we have previously found that L–L adducts are more stable when four-coordinate than when six-coordinate: for example the (L–L)MX$_n$ adducts are not dissociated when M is Zn, Cd or Hg, X is chlorine, and $n = 2$, but are extensively dissociated when M = Sn, X = halogen and $n = 4$ [2c]; in six-coordinated species the fact that tin(IV) halides are strong Lewis acids is outweighed by the steric requirements of the L–L ligand.

Experimental

The samples were dried in vacuo to constant weight (20 °C, ca. 0.1 torr). Carbon, hydrogen, and nitrogen analyses were carried out in this department. The molecular weight determinations were performed at Pascher's Mikroanalytisches Laboratorium, Remagen (F.R.G.). Infrared spectra from 4000 to 250 cm^{-1} were recorded on a Perkin–Elmer 457 instrument. ^{1}H and ^{13}C NMR spectra were recorded an a Varian EM-390 and a VXR-300 spectrometer at room temperature (90 and 20 MHz). The electrical resistance of solutions were measured with a Philips GM-4249 bridge at room temperature. Melting points were measured on a 1A 8100 Electrothermal Instrument: only **2** melts, at 250–252 °C, while **1** and **3** char without melting. All the reactions were carried out under nitrogen.

Bis(pyrazol-1-yl)methanetetracarbonylchromium(0) (1)

A solution of hexacarbonylchromium $Cr(CO)_6$ (0.44 g; 2 mmol), in benzene (30 ml) was mixed with a solution of trimethylamine-*N*-oxide (0.445 g; 4 mmol) in methanol (12 ml); and the mixture was added to a benzene solution (30 ml) of the ligand (0.6 g; 4 mmol) under a stream of nitrogen. After 2 days a green colour appeared and a greenish solid began to separate. After a further day the precipitate was filtered off and washed with methanol and ether. Attempts to recrystallize the compound failed.

Bis(pyrazol-1-yl)methanetetracarbonylmolybdenum(0) (2)

A mixture of a toluene solution (35 ml) of the ligand (0.6 g; 4 mmol) with a toluene solution (25 ml) of hexacarbonylmolybdenum, $Mo(CO)_6$ (0.5 g; 2 mmol), was heated at 70–75 °C (bath temperature) under a stream of nitrogen. A precipitate formed. After 9 h the mixture was placed in the refrigerator, and the greenish-yellow precipitate that appeared was filtered off and washed with ether.

The greenish-yellow tungsten derivative, **3**, was obtained similarly.

An acetone solution (50 ml) of **2** (356 mg; 1 mmol) and 1,2-bis(diphenylphosphino)ethane (398 mg; 1 mmol) was refluxed for 2 h. Upon concentration to small volume and addition of diethyl ether a pale yellow precipitate was obtained and this was filtered off and identified as $(Ph_2PCN_2)_2Mo(CO)_4$ from m.p. (195–197 °C), infrared spectrum (Table 2) and analysis (Found: C, 59.22, H, 3.84. $C_{30}H_{10}N_4O_4P_2$ calc.: C, 59.42; H, 3.88%).

Acknowledgements

We thank the "Consiglio Nazionale delle Ricerche" and the "Ministero della Pubblica Istruzione" for financial support of this investigation, and Mr. V. Amici for technical assistance.

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