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SEVEN-COORDINATE MOLYBDENUM(II) COMPLEXES CONTAINING CARBONYL, TRIPHENYLPHOSPHINE, AND O-DONOR OR S-DONOR ANIONIC BIDENTATE LIGANDS

V. RIERA *,

Departamento de Química Inorgánica, Facultad de Química, Universidad de Oviedo, 33071-Oviedo (Spain)

F.J. ARNAIZ and G.G. HERBOSA

Departamento de Química Inorgánica, Colegio Universitario Integrado, 09002-Burgos (Spain)

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Summary

A series of seven-coordinate molybdenum(II) complexes containing carbonyl, triphenylphosphine, bromide and/or O-donor and S-donor anionic bidentate ligands have been prepared in high yield. The synthesis involves the reaction of the six-coordinate complex $Mo(CO)_2(PPh_3)_2Br_2$ with the sodium salt of the appropriate ligand, in dichloromethane/methanol solution. The new complexes $Mo(CO)_2(PPh_3)_2Br(XOCR)$ ($X = O$, $R = H$, Me, Et, Ph, Cl_3C; $X = S$, $R = Me$, Ph). $Mo(CO)_2(PPh_3)_2(XOCR)_2$ ($X = O$, $R = H$, Me, Et, Ph; $X = S$, $R = Me$, Ph), $Mo(CO)(PPh_3)_2(SOCR)_2$ ($R = Me$, Ph) and $Mo(CO)_2(PPh_3)_2Br(NO_3)$ have been characterized by elemental analysis, IR spectroscopy, and conductivity measurements. An improved synthesis of $Mo(CO)_2(PPh_3)_2(S_2COCH_3)_2$ is described.

Introduction

Although the carbonyl complexes of molybdenum(II) constitute one of the largest classes of seven coordinate derivatives of this element, compounds containing anionic O-donor ligands are relatively scarce. An important group of molybdenum(II) complexes is that formed by compounds containing tertiary phosphine and carbonyls together with various types of sulfur chelating ligands ($R_2NCS_2^-$, $R_2PS_2^-$ and $ROCS_2^-$) [1–5]. On the other hand several mononuclear carbonylmolybdenum(II) compounds, containing anionic O-donor ligands, such as $Mo(OBu^t)_2(CO)_2(py)$ [6], $[Mo(CO)_2(dike)(allyl)Cl]^-$ (dike = β-diketonate) [7] and the 8-quinolinate, picolinate and Schiff base derivatives prepared by Batschelet and his colleagues have been reported [8]. Other seven-coordinate molybdenum(II) complexes *cis*-$[MoX(CO)_2(dmpe)_2]X$ (dmpe = $Me_2PCH_2CH_2PMe_2$; X = NCS or

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NO_3), $[MoX(CO)(NO)(dmpe)_2]$ ($X = NO_2$) and *cis*-$[Mo(OZO_m)(CO)_2(dmpe)_2]$ ($Z = C$, $m = 2$; $Z = S$, $m = 3$) have been synthesized by oxidation of $Mo(CO)_2(dmpe)_2$ with silver salts ($AgNO_2$, Ag_2CO_3, Ag_2SO_4, $AgNO_3$, etc.) [9]. Carboxylate derivatives such as $Mo(CO)_2(allyl)(bipy)(OOCR)$ ($R = Me$, Ph, CF_3, C_2F_5, C_3F_7) [10]. $(\eta^5\text{-}C_5H_5)Mo(CO)_3(OOCCF_3)$ [11], $Mo(OOCCF_3)_2(dppe)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) [12] and $Mo(CNBu^t)_5(OOCMe)_2$ [13] have also been described. The carboxylate ligands in all these compounds show monodentate behaviour.

In this paper we describe a study of the reactivity of the blue 16-electron complex $Mo(CO)_2(PPh_3)_2Br_2$ (I) towards a series of O- or S-donor ligands (carboxylates, thiocarboxylates, acetylacetone, methoxide, methylxanthate or nitrate). The reactivity pattern observed conforms with that of a typical coordinatively unsaturated metal complex, and has led to the preparation of several carbonylmolybdenum(II) compounds containing both bidentate-chelate and monodentate carboxylate ligands. Analogous thiocarboxylate compounds are also described.

Results and discussion

Treatment of a suspension in CH_2Cl_2 of the coordinatively unsaturated complex $Mo(CO)_2(PPh_3)_2Br_2$ (I) with methanolic solutions of sodium carboxylates (NaOOCR) or thiocarboxylates (NaSOCR) in equimolar ratio afforded orange-yellow solutions from which the bromocarboxylates $Mo(CO)_2(PPh_3)_2Br(OOCR)$ (R = H, Me, Et, Ph, Cl_3C) (II–VI) and bromothiocarboxylates $Mo(CO)_2(PPh_3)_2Br(SOCR)$ (R = Me, Ph) (VII–VIII) were isolated as crystals. Reaction of I with sodium nitrate under the same conditions yielded the analogous bromonitrate compound $Mo(CO)_2(PPh_3)_2Br(NO_3)$ (IX).

Addition of a solution of $NaOCH_3$ in MeOH to a CH_2Cl_2 suspension of I in equimolar ratio resulted in decomposition, with formation of *trans*-$Mo(CO)_4(PPh_3)_2$ together with other unidentified non-carbonylic products, but when the reaction was carried out under a CO_2 atmosphere a yellow solution was obtained. From this solution it was possible to isolate an unstable compound for which, on the basis of its IR spectrum (See Experimental), the formula $Mo(CO)_2(PPh_3)_2Br(OOCOCH_3)$ (including methylcarbonate ligand) was suggested. These observations can be tentatively accounted for by assuming that $NaOCH_3$ reacts with CO_2 to give $NaOOCOCH_3$ [14] which subsequently reacts with I. On the other hand, when CS_2 was used instead of CO_2, decomposition, with formation of *trans*-$Mo(CO)_4(PPh_3)_2$, was observed. This suggested that $NaOCH_3$ reacted more quickly with I than with CS_2, since the reaction of I with sodium methylxanthate led in high yield to the known $Mo(CO)_2(PPh_3)(S_2COCH_3)$ (X) without any decomposition. However, it has been reported [2] that $Mo(CO)_2(PPh_3)(S_2COCH_3)_2$ (X) and $Mo(CO)(PPh_3)_2(S_2COCH_3)_2$ are formed simultaneously when $Mo(CO)_3(PPh_3)_2Cl_2$ is treated with sodium methylxanthate.

The reaction between I and sodium acetylacetonate afforded *cis*-$Mo(CO)_4(PPh_3)_2$ in low yield, together with other insoluble non-carbonylic compounds which were not characterized. Similar reduction processes (Mo^{II} to Mo^0) have been observed by other workers [6], and such behaviour seems to be related to the hard base character of the attacking ligands. We cannot suggest, why *trans*-$Mo(CO)_4(PPh_3)_2$ is formed with sodium methoxide and the *cis*-isomer with sodium acetylacetonate.

Formation of the bis-carboxylate $Mo(CO)_2(PPh_3)_2(OOCR)_2$ (R = H, Me, Et, Ph) (XI–XIV) and bis-thiocarboxylate complexes $Mo(CO)_2(PPh_3)_2(SOCR)_2$ (R = Me, Ph) (XV–XVI) were observed when I reacted with the corresponding ligands in a 2/1 ligand/complex I molar ratio. The bis-carboxylate compounds XI–XIV decomposed slowly at room temperature in CH_2Cl_2 but rapidly in refluxing methanol with formation of *trans*-$Mo(CO)_4(PPh_3)_2$. Nevertheless, in refluxing methanol, the bis-thiocarboxylate complexes XV–XVI gave the new monocarbonyls $Mo(CO)(PPh_3)_2(SOCR)_2$ (XVII–XVIII). This different behaviour is probably related to the softer character of the $SOCR^-$ than of the $OOCR^-$ ligands [15].

The IR spectrum of I shows two ν(CO) bands, at 1965 and 1890 cm^{-1}; the OC–Mo–CO angle has a value of 119.4° in this compound as established by X-ray

TABLE 1

ANALYSES AND CONDUCTIVITY DATA

Complex		M.p. (°C)[a]	Analysis (Found (calcd.) (%))				Λ (S cm^2 mol^{-1})[b]
			C	H	Mo	Br	
$Mo(CO)_2(PPh_3)_2Br(OOCH)$	(II)	125	58.20	3.90	11.85	10.01	4.1
			(58.45)	(3.89)	(11.97)	(9.97)	
$Mo(CO)_2(PPh_3)_2Br(OOCCH_3)$	(III)	142	58.62	4.32	11.66	9.84	3.2
			(58.91)	(4.08)	(11.76)	(9.80)	
$Mo(CO)_2(PPh_3)_2Br(OOCH_2CH_3)$	(IV)	148	59.16	4.39	11.48	9.66	3.4
			(59.37)	(4.37)	(11.56)	(9.63)	
$Mo(CO)_2(PPh_3)_2Br(OOCC_6H_5)$	(V)	143	61.45	3.95	10.84	9.21	4.1
			(61.59)	(4.02)	(10.93)	(9.10)	
$Mo(CO)_2(PPh_3)_2Br(OOCCCl_3)$	(VI)	157	52.05	3.35	10.37	–	3.8
			(52.29)	(3.29)	(10.44)		
$Mo(CO)_2(PPh_3)_2Br(SOCCH_3)$	(VII)	155	60.80	4.35	11.44	9.60	4.0
			(61.02)	(4.39)	(11.54)	(9.60)	
$Mo(CO)_2(PPh_3)_2Br(SOCC_6H_5)$	(VIII)	191	62.45	4.05	–	–	3.9
			(62.65)	(4.09)			
$Mo(CO)_2(PPh_3)_2Br(NO_3)$ [c]	(IX)	138	55.40	3.80	11.65	9.70	3.4
			(55.76)	(3.69)	(11.72)	(9.76)	
$Mo(CO)_2(PPh_3)(S_2COCH_3)_2$	(X)	176	45.75	3.30	–	–	3.0
			(45.86)	(3.37)			
$Mo(CO)_2(PPh_3)_2(OOCH)_2$	(XI)	96	62.53	4.15	12.29	–	4.2
			(62.65)	(4.21)	(12.51)		
$Mo(CO)_2(PPh_3)_2(OOCCH_3)_2$	(XII)	115	63.05	4.65	11.90	–	3.8
			(63.48)	(4.57)	(12.07)		
$Mo(CO)_2(PPh_3)_2(OOCCH_2CH_3)_2$	(XIII)	118	64.17	4.98	11.45	–	4.3
			(64.24)	(4.90)	(11.66)		
$Mo(CO)_2(PPh_3)_2(OOCC_6H_5)_2$	(XIV)	120	67.67	4.05	10.25	–	4.5
			(67.98)	(4.39)	(10.44)		
$Mo(CO)_2(PPh_3)_2(SOCCH_3)_2$	(XV)	132	60.90	4.33	–	–	4.0
			(61.02)	(4.39)			
$Mo(CO)_2(PPh_3)_2(SOCC_6H_5)_2$	(XVI)	148	65.46	4.30	–	–	3.7
			(65.68)	(4.24)			
$Mo(CO)(PPh_3)_2(SOCCH_3)_2$	(XVII)	190	61.35	4.45	–	–	4.1
			(61.58)	(4.54)			
$Mo(CO)(PPh_3)_2(SOCC_6H_5)_2$	(XVIII)	203	66.02	4.24	–	–	3.8
			(66.37)	(4.37)			

[a] All melted with decomposition. [b] In acetone (ca. 10^{-3} *M*). [c] N: found 1.68, calcd. 1.71%.

crystallography [16]. All the derivatives $Mo(CO)_2(PPh_3)_2Br(OOCR)$ (II–VI), $Mo(CO)_2(PPh_3)_2(OOCR)_2$ (XI–XIV), $Mo(CO)_2(PPh_3)_2Br(NO_3)$ (IX) (Table 2) and the $Mo(CO)_2(PPh_3)_2Br(OOCOCH_3)$ (bromo-methylcarbonate) complex show two bands due to the C–O stretching vibrations of the two CO groups. From the relative intensities of the bands for solutions, approximate values of 130° can be estimated for the OC–Mo–CO angle in these compounds. However, the thiocarboxylate derivatives VII–VIII and XV–XVI showed two bands with similar intensities, which is characteristic of OC–Mo–CO angles of 90° [17].

The $\nu(CO)$ frequencies in the monocarboxylate derivatives II–VI and IX decreased with the acidity of the RCOOH ($Cl_3CCOO^- > HCOO^- > PhCOO^- > EtCOO^- = MeCOO^-$), showing for the nitrate complex IX the greatest values because NO_3^- is the weakest base. The bis-carboxylate complexes XI–XIV seems to follow the same trend, but the $\nu(CO)$ frequencies are lower than for the corresponding bromo-carboxylates because bromide has been replaced by a strong base.

The differences between $\nu(COO)_{asym}$ and $\nu(COO)_{sym}$ stretching frequencies, denoted Δ, are generally useful in distinguishing between monodentate and bidentate behaviour of carboxylates [18]. If Δ values similar to or smaller than those showed by NaOOCR are found, it is characteristic of a bidentate (chelating or bridging) carboxylate. The Δ values found in $Mo(CO)_2(PPh_3)_2Br(OOCR)$ (II–VI) correspond (see Table 2) to bidentate behaviour. The molecular weight of acetato complex III (Found 790 g mol^{-1}; calcd. for the monomer 815 g mol^{-1}) confirmed

TABLE 2

IR AND UV-VIS SPECTROSCOPIC DATA

Complex		$\nu(CO)$ [a] (cm^{-1})	ν_{asym}-(CO_2) [b]	ν_{sym}-(CO_2) [b]	Δ	λ(nm) [a]
$Mo(CO)_2(PPh_3)_2Br(OOCH)$	(II)	1958,1870	1540	1380	160	445
$Mo(CO)_2(PPh_3)_2Br(OOCCH_3)$	(III)	1952,1864	1530	1450	80	434
$Mo(CO)_2(PPh_3)_2Br(OOCCH_2CH_3)$	(IV)	1952,1864	1520	1450	70	432
$Mo(CO)_2(PPh_3)_2Br(OOCC_6H_5)$	(V)	1952,1868	1510	1420	90	435
$Mo(CO)_2(PPh_3)_2Br(OOCCCl_3)$	(VI)	1960,1872	1588	1402	186	442
$Mo(CO)_2(PPh_3)_2Br(SOCCH_3)$	(VII)	1938,1860	–	–	–	430
$Mo(CO)_2(PPh_3)_2Br(SOCC_6H_5)$	(VIII)	1940,1864	–	–	–	420
$Mo(CO)_2(PPh_3)_2Br(NO_3)$	(IX)	1962,1881	–	–	–	444
$Mo(CO)_2(PPh_3)(S_2COCH_3)_2$ [c]	(X)	1960,1870	–	–	–	470
$Mo(CO)_2(PPh_3)_2(OOCH)_2$	(XI)	1951,1863	1540	1380	160	423
			1620	1285	335	
$Mo(CO)_2(PPh_3)_2(OOCCH_3)_2$	(XII)	1944,1855	1530	1450	80	411
			1618	1370	248	
$Mo(CO)_2(PPh_3)_2(OOCCH_2CH_3)_2$	(XIII)	1944,1858	1520	1450	70	412
			1590	1388	202	
$Mo(CO)_2(PPh_3)_2(OOCC_6H_5)_2$	(XIV)	1949,1862	1510	1420	90	–
			1620	1350	270	
$Mo(CO)_2(PPh_3)_2(SOCCH_3)_2$	(XV)	1948,1861	–	–	–	485
$Mo(CO)_2(PPh_3)_2(SOCC_6H_5)_2$	(XVI)	1948,1865	–	–	–	–
$Mo(CO)(PPh_3)_2(SOCCH_3)_2$	(XVII)	1778	–	–	–	480
$Mo(CO)(PPh_3)_2(SOCC_6H_5)_2$	(XVIII)	1778	–	–	–	474

[a] In dichloromethane. Molar absorptivities were in the range 400–900 dm^3 mol^{-1} cm^{-1}. [b] In KBr pellets. [c] This complex was previously known.

that these are mononuclear in solution. Therefore, the bromocarboxylate complexes II–VI must be considered as seven coordinated monomers of molybdenum(II), with the carboxylate ligand acting as a chelate. The nitrate complex IX showed three bands at 1512, 1219 and 1015 cm^{-1}; this is consistent with the presence of a bidentate chelate nitrate ligand [19], which also raises the coordination at Mo to seven.

All the bis(carboxylate) complexes XI–XIV exhibit the same pattern for the bands from the (COO) groups, showing chelated and monodentate carboxylate simultaneously. Thus, for example, $Mo(CO)_2(PPh_3)_2(OOCMe)_2$ (XII) showed $\nu(COO)_{asym}$ and $\nu(COO)_{sym}$ at 1530 and 1450 cm^{-1} (Δ 80 cm^{-1}) corresponding to chelate acetate, along with bands at 1618 and 1370 cm^{-1} (Δ 248 cm^{-1}) that can be attributed to monodentate acetate (see Table 2).

In the case of bromothiocarboxylate complexes $Mo(CO)_2(PPh_3)_2Br(SOCR)$ (VII–VIII) it was not easy to assign bands, but the thiobenzoate derivative VIII showed two absorptions, at 1480 and 968 cm^{-1}, which are assignable respectively [20] to the $\nu(CO)$ and $\nu(CS)$ stretching of a thiobenzoate group acting as a bidentate chelate ligand.

The bis-thiocarboxylate $Mo(CO)_2(PPh_3)_2(SOCR)_2$ compounds XV–XVI showed an additional band at ca. 1600 cm^{-1}, which suggested that the second thiocarboxylate group was coordinated through the sulfur atom. Finally, no band at 1600 cm^{-1} was found in the IR spectra of $Mo(CO)(PPh_3)_2(SOCR)_2$ (XVII–XVIII), in which presumably both thiocarboxylate ligands are bidentate.

It is evident that our results are compatible with seven coordination for molybdenum(II) in all the complexes.

The analytical, conductivity, and spectroscopic data (IR and UV-VIS) are given in Tables 1 and 2.

Experimental

Preparations were carried out under dry argon. The complex $Mo(CO)_2(PPh_3)_2Br_2$ (I) [21] was prepared by a published method. IR spectra were recorded with a Perkin–Elmer 577 spectrophotometer. UV-VIS spectra were recorded with a Perkin–Elmer 554 spectrophotometer. Conductivity measurements were made with a WTW conductivity bridge LBR at 3 kHz; the cell constant of the glass conductivity probe was determined by use of 0.01 mol dm^{-3} KCl solution. Elemental analysis for C, H, N, were determined with a Carlo Erba 1106 or a Perkin–Elmer 240 instrument. Molybdenum was determined as its 8-hydroxyquinolinate [22] and bromide by potentiometric titration against standard $AgNO_3$ solution after the compounds had been fused carefully with $NaOH/Na_2O_2$ mixture.

$Mo(CO)_2(PPh_3)_2Br(XOCR)$ ($X = O$, $R = H$, Me, Et, Ph, Cl_3C; $X = S$, $R =$ Me, Ph) (II–VIII)

To a suspension of $Mo(CO)_2(PPh_3)_2Br_2$ (I) (0.24 mmol) in CH_2Cl_2 (40 ml) was slowly added a solution of the ligand NaXOCR (0.24 mmol) in MeOH (10 ml). The mixture was then stirred for 15 min at room temperature. (With $NaSOCCH_3$ and $NaSOCC_6H_5$, freshly prepared solutions must be used.) The resulting orange-yellow solutions were concentrated to ca. 20 ml by evaporation under reduced pressure. Addition of MeOH (20 ml) and subsequent concentration gave crystals, which were washed with methanol and diethyl ether, then dried in vacuo. Yields 80–90%.

$Mo(CO)_2(PPh_3)_2Br(NO)_3$ (IX)

Complex IX was prepared similarly by use of 0.24 mmol of $NaNO_3$ in 10 ml of MeOH. Yield 87%.

$Mo(CO)_2(PPh_3)_2(XOCR)_2$ (X = O, R = H, Me, Et, Ph; X = S, R = Me, Ph) (XI–XVI)

To a suspension of $Mo(CO)_2(PPh_3)_2Br_2$ (I) (0.24 mmol) in CH_2Cl_2 (40 ml) was slowly added a solution of NaXOCR (0.48 mmol) in MeOH (20 ml). After 15 min stirring at room temperature the mixture was evaporated to 30 ml. Methanol (30 ml) was added and the solution was concentrated under reduced pressure. The crystals obtained were washed with methanol and diethyl ether then dried in vacuo. Yields 70–80%.

$Mo(CO)(PPh_3)_2(SOCR)_2$ (R = Me, Ph) (XVII–XVIII)

To a suspension of $Mo(CO)_2(PPh_3)_2Br_2$ (I) (0.6 mmol) in MeOH (20 ml) was added a freshly prepared solution of NaSOCR (1.5 mmol) in MeOH (25 ml). The mixture was refluxed for 30 min, then cooled to room temperature to give dark crystals, which were washed with methanol and diethyl ether. Yields 21–25%.

$Mo(CO)_2(PPh_3)(S_2COMe)_2$ (X)

To a suspension of $Mo(CO)_2(PPh_3)_2Br_2$ (I) (0.24 mmol) in CH_2Cl_2 (20 ml) was slowly added a solution of NaS_2COMe (0.48 mmol) in MeOH (20 ml). After 15 min stirring at room temperature the solution was evaporated to dryness under reduced pressure. The orange solid was dissolved in CH_2Cl_2 and the solution was filtered, then evaporated in vacuo. The solid obtained was washed with hexane until free from PPh_3, and then recrystallized from diethyl ether. Yield 90%.

Reaction of I with $NaOCH_3$ in an atmosphere of CO_2

A stream of CO_2 was passed through a suspension of $Mo(CO)_2(PPh_3)_2Br_2$ (I) (0.24 mmol) in CH_2Cl_2 (40 ml). A solution of $NaOCH_3$ (0.24 mmol) in MeOH (10 ml) was then slowly added; the blue colour changed to yellow. Evaporation under reduced pressure (the Schlenk tube being filled with CO_2 from time to time) gave yellow crystals, which were very unstable outside the CO_2 atmosphere, and only solid IR spectra (in KBr pellet) could be obtained. $\nu(CO)$ in CH_2Cl_2 solution (cm^{-1}): 1952, 1868. $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$ in KBr pellet (cm^{-1}): 1560, 1370.

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