Inorganica Chimica Acta, 127 (1987) L17–L18

Semicarbazone Allyl Dicarbonyl Complexes of Molybdenum(II)

MICHEL J. M. CAMPBELL*, ELIZABETH MORRISON, VERNON ROGERS

School of Chemistry, Thames Polytechnic, Wellington Street, London SE18 6PF, U.K.

and PAUL K. BAKER*

Department of Chemistry, University College of North Wales, Bangor, Gwynedd LL57 2UW, U.K.

(Received September 15, 1986)

Although semicarbazones have been used as bidentate ligands in 'classical' coordination chemistry [1], hitherto there have been no reported examples of organometallic compounds containing these as attached ligands. Semicarbazones have been found to be useful as anti-convulsants [2], as well as being shown to have anti-phytoviral [3] and anti-implantation [4] activity.

We now wish to report the synthesis of the new complexes $[MoX(CO)_2\{(R',R'')CNNHCONH_2\}(\eta^3\text{-}C_3H_4R)]$ (X = Cl, Br or I; R′,R″ = H, Me, Et, ^{n}Pr, Ph; R = H or Me) which are the first organotransition-metal complexes (and also the first d^4 compounds) containing a semicarbazone as a bidentate ligand coordinated to molybdenum.

Results and Discussion

Equimolar quantities of the semicarbazone $(R',R'')CNNHCONH_2$ (R′,R″ = H, Me, Et, ^{n}Pr, Ph) and $[MoX(CO)_2(NCMe)_2(\eta^3\text{-}C_3H_4R)]$ (X = Cl, Br or I, R = H or Me) react in CH_2Cl_2 to afford, upon precipitation with diethylether, the bright yellow complexes $[MoX(CO)_2\{(R',R'')CNNHCONH_2\}(\eta^3\text{-}C_3H_4R)]$ in high yields. The compounds are only sparingly soluble in dichloromethane and trichloromethane, but are much more soluble in dimethylsulphoxide. They are stable in the solid state when stored under nitrogen, but decompose rapidly in solution. The complexes have been fully characterised by elemental analysis (C, H and N) and IR spectroscopy (Table I) and by ^{1}H NMR spectroscopy (Table II).

From a comparison of the NMR data of the coordinated and free semicarbazones the only significant changes in chemical shift are for the NH and NH_2 group. This would be expected since both the NH and NH_2 groups are attached to the directly coordinated carbonyl (CO) and hydrazine (CN) groups. The shift is appreciably greater for the NH group which is attached to both groups.

It is highly likely that the geometry of the complexes are octahedral (assuming that the π-allyl group occupies one coordination site) with the π-allyl group and the halide *trans* to each other since X-ray structural analysis on the analogous complexes with attached bidentate nitrogen [5] and oxygen [6] ligands show this geometry. The infrared (Table I) and ^{1}H NMR data (Table II) support this geometry for the semicarbazone complexes (Fig. 1). In the infrared spectrum *trans*-carbonyl li-

TABLE I. Yields, Analytical (C, H and N)[a] and IR[b] Data of the Complexes $[MoX(CO)_2\{(R',R'')CNNHCONH_2\}(\eta^3\text{-}C_3H_4R)]$

	Yield (%)	C	H	N	ν(CO) (cm^{-1})	ν(CO) (cm^{-1}) SCone
1 $\{MoI(CO)_2\{(CH_3)_2CNNHCONH_2\}(\eta^3\text{-}C_3H_5)]$	76	24.6(24.8)	3.1(3.3)	9.6(9.7)	1945s 1850s	1665s
2 $[MoCl(CO)_2\{(CH_3\text{–},CH_3CH_2\text{–})CNNHCONH_2\}(\eta^3\text{-}C_3H_5)]$	72	33.6(33.6)	4.5(4.5)	11.8(11.8)	1940s 1845s	1660s
3 $[MoI(CO)_2\{(CH_3\text{–},CH_3CH_2\text{–})CNNHCONH_2\}(\eta^3\text{-}C_3H_5)]$	73	26.0(26.7)	3.5(3.6)	9.0(9.4)	1924s 1850s	1660s
4 $[MoCl(CO)_2\{(CH_3\text{–},CH_3CH_2\text{–})CNNHCONH_2\}(\eta^3\text{-}C_3H_4Me\text{-}2)]$	40	35.5(35.5)	4.9(4.9)	11.4(11.3)	1938s 1840s	1660s
5 $[MoCl(CO)_2\{(CH_3\text{–},CH_3CH_2CH_2\text{–})CNNHCONH_2\}(\eta^3\text{-}C_3H_5)]$	75	33.1(33.6)	4.5(4.5)	11.5(11.8)	1945s 1848s	1658s
6 $[MoBr(CO)_2\{(C_6H_5)CHNNHCONH_2\}(\eta^3\text{-}C_3H_5)]$	86	35.8(35.8)	3.3(3.2)	9.8(9.6)	1935s 1855s	1661s

[a] Calculated values in parentheses. [b] Spectra recorded as a KBr disc, s, strong.

---

*Authors to whom correspondence should be addressed.

0020-1693/87/$3.50

TABLE II. ^{1}H NMR Data (δ)[a] of the Complexes $[MoX(CO)_2\{(R',R'')CNNHCONH_2\}(\eta^3\text{-}C_3H_4R)]$ and the Semicarbazones [a]Spectra were recorded in d^6 dimenthylsulphoxide at 25 °C using $SiMe_4$ as a reference. s, singlet; d, doublet; t, triplet; q, quartet;

	CH_α allylic[b]	R[c]	R′	R″				
				CH_3–	–CH_2–	–CH_2–	NH_2	NH
1	1.08d (J = 2.0 Hz)		1.86s				6.15s	8.83s
2	1.08d (J = 2.1 Hz)		1.73s	1.00t (J = 1.9 Hz)	2.15q (J = 1.90 Hz)		6.15s	8.85s
3	1.08d (J = 2.0 Hz)		1.76s	1.00t (J = 1.9 Hz)	2.16q (J = 1.9 Hz)		6.16s	8.86s
4	0.84d (J = 0.9 Hz)	1.91d (J = 0.2 Hz)	1.76s	1.00t (J = 1.9 Hz)	2.16q (J = 1.9 Hz)		6.16s	8.86s
5	1.08d (J = 1.5 Hz)		1.76s	0.86t (J = 1.9 Hz)	1.48q (J = 1.9 Hz)	2.12t (J = 1.9 Hz)	6.14s	8.84s
6	1.08d (J = 2.2Hz)		7.83s	7.31–7.40m(3H)	7.70–7.72m(2H)		6.49s	10.25s
7			1.78s	1.01t (J = 2.5 Hz)	2.16q (J = 2.5 Hz)		6.26s	8.99s[d]
8			1.76s	0.86t (J = 2.7 Hz)	1.50q (J = 2.7 Hz)	2.14t (J = 2.9 Hz)	6.21s	8.97s[d]

[a] Spectra were recorded in d^6 dimethylsulphoxide at 25 °C using $SiMe_4$ as a reference. s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. [b] CH_β allylic resonances have been found to occur at $\delta \doteq 3.5$ (under dimethylsulphoxide) [7]. [c] When R = H the resonance appears as a broad multiplet due to geminal coupling which cannot often be detected [7]. [d] Free semicarbazones.

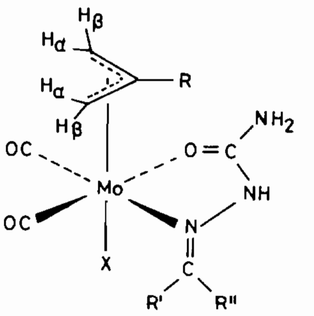

Fig. 1. The geometry of the complexes $[MoX(CO)_2\{(R',R'')CNNHCONH_2\}(\eta^3\text{-}C_3H_4R)]$.

gands would show a high intensity band (symmetric stretch) and a low intensity band (asymmetric stretch). Since this is not the case, the carbonyl ligands are thought to be *cis* to each other.

We are currently investigating the chemistry of these complexes in detail.

Acknowledgement

We wish to thank Dr O. Howarth at the University of Warwick for high field NMR measurements.

References

1 S. Padhyé and G. B. Kauffman, *Coord. Chem. Rev., 63,* 127 (1985).
2 M. J. Kornet and J. Yeou-Ruoh Chu, *J. Pharm. Sci., 72,* 1213 (1983).
3 G. Schuster, L. Heinisch, W. Schulze, H. Ulbricht and H. Willitzer, *Phytopathology 2, 111,* 97 (1984).
4 K. Nagarajun, P. K. Talwalker, C. L. Kulkarni, A. Venkateswarla, S. S. Prabhee and C. V. Nayak, *Indian J. Chem., 23B,* 1243 (1984).
5 A. J. Graham and R. H. Fenn, *J. Organomet. Chem., 17,* 405 (1969).
6 A. J. Graham and R. H. Fenn, *J. Organomet. Chem., 25,* 173 (1970).
7 H. Tom Dieck and H. Friedel, *J. Organomet. Chem., 14,* 375 (1968).