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Synthesis of new stereochemically non-rigid molybdenum-allyl complexes containing the bis(3,5-dimethylpyrazolyl)methane ligand *

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Abstract

A convenient preparation of $LMo(CO)_4$ (L = bis(3,5-dimethylpyrazolyl)methane) and the syntheses of several fluxional *cis*-$LMo(CO)_2$(allyl) compounds are reported. Their proton NMR spectra are discussed.

Introduction

Polypyrazolyl ligands have been increasingly used in organometallic and coordination chemistry in recent years [1]. Interest in this class of ligands stems from their ability to modify the reactivity pattern of metal complexes when compared with that of complexes containing polypyridyl, polyphosphino, or cyclopentadienyl ligands. Although Trofimenko originally introduced the polypyrazolylborates as a class of versatile uninegative bidentate or tridentate ligands, he foresaw the potential of related ligands in which the boron is replaced by another element [2]. Replacement of boron by carbon provided a class of neutral polypyrazolyl chelating ligands [3]. The chemistry of Group VI metals (Cr, Mo and W) containing these ligands has been widely studied [4,5] in recent years.

We describe here an efficient mild-conditions synthesis of bis(3,5-dimethyl-1-pyrazolyl)methanemolybdenum(0)tetracarbonyl (**2**) [4], and the preparation of some new π-allyl complexes containing this ligand which exhibit stereochemical non-rigidity.

Results and discussion

In the reactions of bis(3,5-dimethyl-1-pyrazolyl)methane (**1**) with Group VI metal carbonyls the ligand is usually heated with the metal carbonyl in 1,2-dimethoxy-

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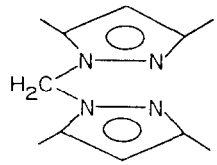

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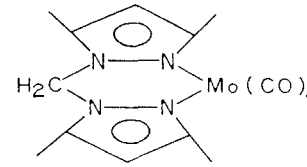

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Fig. 1.

ethane [4a] or toluene [5] for several hours. Oxidative decarbonylation with an amine *N*-oxide [6] is a useful alternative to thermolysis for such ligand substitution, since it can be carried out at ambient temperature.

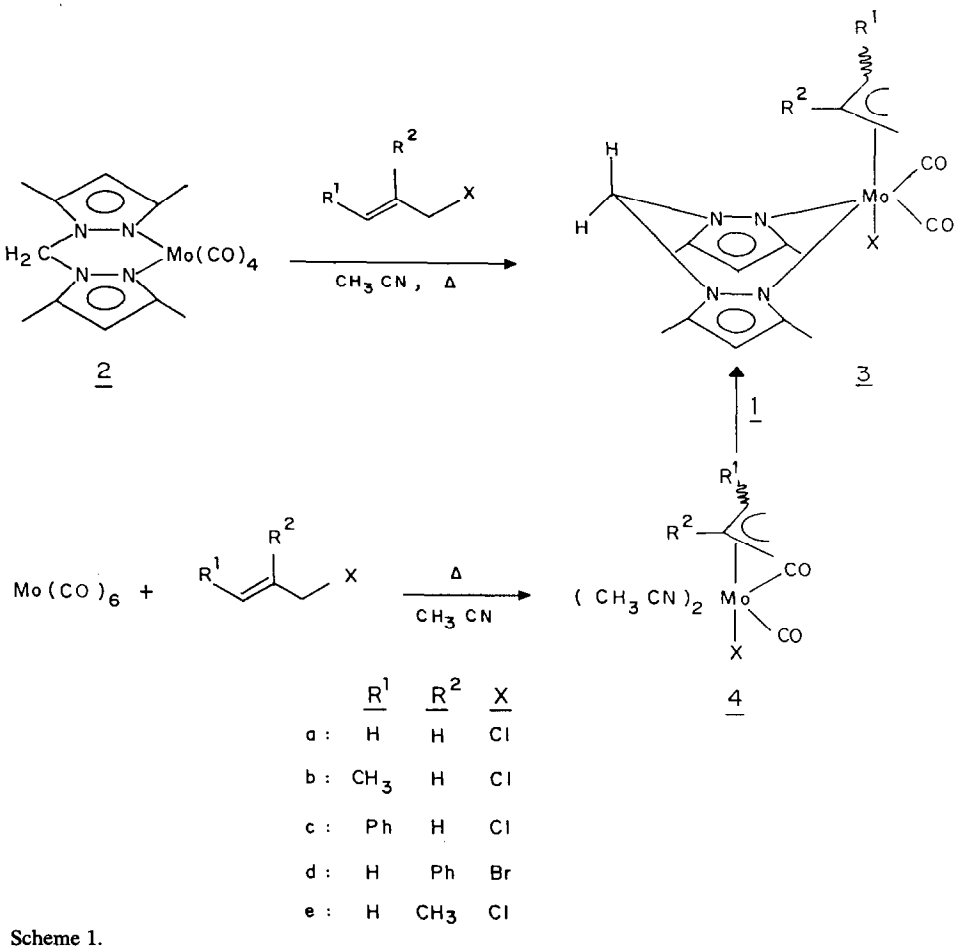
In the presence of trimethylamine-*N*-oxide (2 equiv.), $Mo(CO)_6$ smoothly reacts with bis(3,5-dimethyl-1-pyrazolyl)methane (**1**) in benzene at room temperature to give the tetracarbonylmolybdenum complex **2** (Fig. 1) in 59% yield. We found that the product was slightly air-sensitive, as previously reported [4a], but it can be stored in the freezer for several months. Its identity was confirmed by the characteristic carbonyl absorptions (Table 1). The solid state ^{13}C (MAS) NMR spectrum revealed two sets of CO peaks (224, 221 and 208, 207 ppm) indicating a lower symmetry in this species than in the corresponding 1,10-phenanthroline or 2,2′-bipyridyl complexes [7]; for these latter compounds there are only two peaks (*cis* and *trans*) for the carbonyl resonances (223 and 205, 223 and 207 ppm, respectively) in the solid state. The non-degeneracy of the carbonyl resonances for compound **2** is apparent from its X-ray structure [4b], which shows four dissimilar CO groups in the solid state.

Table 1

Physical, infrared (Nujol) and microanalytical [a] data

Compound	Color	Dec. temp. (°C)	Yield (%)	C=O (cm^{-1})	C=N (cm^{-1})	Anal. Found (calcd.) (%)	
						C	H
2	greenish yellow	170	59	2000 1910 1870 1810	1560	43.61 (43.68)	3.77 (3.88)
3a	yellow	232	72	1910 1810	1550	44.39 (44.39)	4.33 (4.85)
3b	yellow	236	78	1950 1830	1560	45.59 (45.68)	5.52 (5.15)
3c	orange	225	60	1920 1830	1555	51.53 (51.91)	5.25 (4.91)
3d	yellow	219	35	1940 1860	1560	46.83 (47.73)	4.55 (4.52)
3e	yellow	–	–	1920 1830	1560	–	–

[a] Elemental analyses were performed at the Regional Sophisticated Instrumentation Centre, Punjab University, Chandigarh.



Scheme 1.

When a solution of compound **2** and allyl, crotyl or cinnamyl chloride in acetonitrile was heated for 5–6 h, the corresponding allyl complexes **3a–c** were obtained in moderate yields (Scheme 1). These complexes were obtained in better yields by ligand exchange of allyl complexes **4a–c** with **1**. The spectral and analytical data are presented in Table 1 and Table 2. An analogous complex derived from allyl bromide was previously reported by Shiu [4a]. Except for **3e**, the π-allyl complexes are stable solids which can be handled in air, but their solutions are unstable.

The reaction of compound **2** with 2-methallyl chloride under similar conditions did not yield the expected π-allyl complex **3e**, and instead a dark brown crystalline solid separated when the solution was kept overnight at room temperature. The same product was obtained when **4e** was treated with the **1** and the solution kept at room temperature overnight. The methallyl complex **3e** was finally isolated by a different choice of conditions when complex **4e** was treated with a solution of ligand **1** in methanol at room temperature. Complex **3e** separated as a yellow solid and was filtered off. It survived just long enough to allow its IR and ^{1}H NMR spectra to be

Table 2

^{1}H NMR data [a] (ppm, in $CDCl_3$, TMS as internal standard)

Compound	Me-pz		H-pz	CH_2		Allyl signals			
						syn	*anti*	1-sub	2-sub
2	2.45	2.4	5.95	5.9–6.4					
	s	s	s	m					
3a	2.25	2.5	5.85	5.8–6.0	3.4	1.35	–	4.25	
	s	s	s	m	d	d		m	
3b [b]	2.3	2.6	5.9	6.0	6.6	(4.2, 4.7, 3.4, 1.0)		1.2	–
						m m m m		s	
3c [c]	2.0	2.3	5.95	5.7		3.1	1.15	7.3	4.1
	s	s	s	s		d	d	m	m
3d	2.1	2.3	5.85	3.4	4.7	3.7	1.4		7.15
	s	s	s	d	d	s	s		m
3e	2.2	2.45	6.0	5.8		3.1	1.5		1.95
	s	s	s	d		bs	bs		s

[a] The CH_2 *geminal* coupling is 16 Hz. For *vicinal* allyl protons, $J = 9.6$ Hz. [b] The allyl protons (in parentheses) could not be individually assigned because of complex dynamic spectrum. Only major peaks have been included. [c] Recorded in DMSO-d_6.

recorded. A solution of **3e** in acetonitrile or dichloromethane darkened almost immediately and yielded dark brown crystals mentioned above when stored overnight in the presence or absence of air. Even as a solid, the compound turned into a dark pasty mass within 0.5 h. In the reaction of 2-phenylallyl bromide with **2**, although the expected allyl complex **3d** was isolated as a stable product, a different dark brown crystalline compound (without allyl and carbonyl moieties, and similar to the unexpected compound described above) separated from the mother liquor on prolonged storage *. Two characteristic strong CO absorptions of equal intensity appeared in the IR spectra of these compounds indicating their *cis* orientation (Table 1).

The ^{1}H NMR spectra of the complexes **3a–e**, which are sparingly soluble in $CDCl_3$ or DMSO-d_6, reveal that they are stereochemically non-rigid. For the 2-phenylallyl compound **3d**, the CH_2 group of the ligand shows two distinct AB signals with geminal coupling of 16 Hz. The chemical shifts of these signals (4.7 and 3.4 ppm) reflect a very large shielding effect by the proximal aromatic ring; in the case of other compounds these methylene protons appeared as a broad singlet around 5.8–6.0 ppm. The large anisotropic shift observed for the methylene protons

* These brown species have identical NMR and IR spectra, indicating that they are isostructural, differing only in the halogen atom. From the Raman spectra and XPES, which are also very similar, it appears that the complexes could be dimeric, containing Mo–Mo multiple bonds [S.A. Best, T.J. Smith and R.A. Walton, *Inorg. Chem.*, 17 (1978) 99]. X-Ray structural determinations are being undertaken to establish the structures unequivocally. Formation of side-products in such reactions are known [B.J. Brisdon, M. Cartwright, D.A. Edwards and K.E. Paddick, *Inorg. Chim. Acta*, 40 (1980) 191; B.J. Brisdon and K.E. Paddick, *J. Organomet. Chem*, 149 (1978) 113]. However, in those cases the compounds contained both the allyl and the CO ligands, unlike those in the present study. We believe pyrazole plays a role in this facile dimerisation.

in **3d** also means that the pyrazoles occupy the equatorial positions and the allyl group occupies an apical position of the distorted octahedral structure. If the appearance of AB pattern is diagnostic of slow interconversion (boat–chair–boat) of the six-membered chelate [8], it follows that this intramolecular motion is fast on NMR time-scale for all the compounds except **3d**. It is relevant to recall with bis(3,5-dimethylpyrazolyl)methane, **1** as a ligand the ring-inversion is slower for steric reasons compared with that of dipyrazolylmethane when the ligand is present on a palladium or platinum halide complex [8]. For the molybdenum π-allyl complexes described here the situation is more complicated.

A second type of intramolecular motion must be considered in these systems, viz. pseudorotation (trigonal twist [9a]) of the two pyrazoles and the halogen, resulting in non-equivalence of the pyrazole groups as well as the allyl protons [9b,c]. Unlike in **3c** and **3d**, the allyl signals are broad in **3a**, **3b** and **3e**, indicating slow exchange, presumably via pseudorotation. A detailed structural study of these new π-allyl complexes of molybdenum will be reported in due course.

Experimental

All reactions were performed under argon, though solutions were exposed to air during work up. The IR spectra were recorded on a Perkin–Elmer 599B instrument as Nujol mulls. The ^{1}H NMR spectra were recorded on Bruker WH-90 and Varian 80A spectrometers. Solid state ^{13}C NMR spectra were recorded on a Bruker MSL 300 instrument operating at 75.5 MHz; chemical shifts were recorded by reference to the methine carbon resonance of adamantane at 37.8 ppm (external standard). Elemental analyses were performed at the Regional Sophisticated Instrumentation Centre, Chandigarh, India, using a Carlo Erba 1106 instrument. Molybdenum hexacarbonyl was purchased from Fluka or Aldrich and used as received. Acetonitrile was freshly distilled over P_2O_5 under argon before use. Trimethylamine *N*-oxide was prepared by a published procedure [10]. Allyl chloride and 2-methallyl chloride were purchased from BDH/Fluka. Crotyl chloride [11], cinnamyl chloride [12], and 2-phenylallyl bromide [13] were prepared by known routes. All the allyl halides were distilled prior to use.

*Bis(3,5-dimethyl-1-pyrazolyl)methane (**1**)*

A mixture of 3,5-dimethylpyrazole (7.68 g, 80 mmol) and dibromomethane (8 g, 44 mmol) in benzene (80 ml) was added to a solution of sodium hydroxide (9 g) in water (9 ml), and tetrabutylammonium bromide (100 mg) was then added. The two-phase mixture was stirred vigorously and heated under reflux for 4 h then cooled to room temperature. The sodium bromide was filtered off and washed with benzene. The benzene layer was separated and evaporated, and the white solid residue was recrystallized from hot petroleum ether (60–80 °C) to afford pure **1** (7.9 g, 96%), m.p. 105 °C (lit. [14] 105 °C).

*Bis(3,5-dimethyl-1-pyrazolyl)methanetetracarbonylmolybdenum (**2**)*

To a stirred suspension of $Mo(CO)_6$ (1.05 g, 4 mmol) in benzene (120 ml) was added a solution of trimethylamine *N*-oxide (1 g, 13.3 mmol) in dry methanol (15 ml). Bis(3,5-dimethyl-1-pyrazolyl)methane (**1**) (1 g, 4.9 mmol) was added in one portion and the mixture was stirred under argon at room temperature for 18 h. The slightly turbid yellow solution was concentrated to about 20 ml and filtered. After

addition of methanol (3 ml) to the filtrate, it was cooled to 0 °C to afford yellow crystals, which were filtered off and dried. The yield was 0.982 g (59.6%).

*General procedure for the preparation of π-allyl complexes (**3a–d**)*

$Mo(CO)_6$ and the allyl halide were refluxed in acetonitrile for 5 h. To the resulting orange or orange-red solution ligand **1** in acetonitrile was added from a syringe, and reflux was continued for 10 more minutes. The solution was kept in the freezer overnight to give the product as crystals in the following yields (2–3 mmol scale): **3a** 72.6%, **3b** 78%, **3c** 60%, and **3d** 35%.

Preparation of complex 3e

The bis-acetonitrile complex **4e** (0.1 g, 0.3 mmol) was stirred with the ligand **1** (0.15 g, 0.735 mmol) in MeOH (10 ml) for 10 min at room temperature, during which the colour of the solution darkened. After partial evaporation of the solvent a small amount of solid separated in the flask, and was quickly filtered off to give 21 mg of complex **3e**. The product turned into a dark brown mass within 30 min at room temperature.

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