

Syntheses and Structure Determination of Allyl Complexes of Molybdenum

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(Received 13th August, 2002, revised 23rd September, 2002)

Summary: The syntheses and characterization of molybdenum tetracarbonyl complexes of pyridyl amine Schiff's base ligands of type $[Mo(CO)_4N^*N]$ are described. These have been prepared by the reaction of *cis*- $[M(CO)_4(pip)_2]$ with the Schiff base ligands. The crystal structures of the $[Mo(CO)_4\{N(Me)=C(Me)C_3H_4N\}]$ and $[Mo(CO)_4\{N(Me)-C(Ph)C_3H_4N\}]$ have also been determined.

Introduction

The synthesis and reactivity of molybdenum tetracarbonyl compound of the type *cis*- $[M(CO)_4L_2]$ with α -diimine nitrogen donor ligands has been well studied [1,2]. Examples of α -diimine ligands include 2,2'-bipyridyl (bipy), 1,10-phenanthroline (phen), 1,4-diazabutadiene (DAB), and pyridyl amine Schiff base. Figure 1 shows the general molecular structure of these ligands. These are π acceptor ligands and accept π -electron density from the metal into ligand π^* -orbitals.

The bipyridyl compounds, *cis*- $[M(CO)_4(bipy)]$ (M = Cr, Mo, W) had been previously prepared by direct reaction with metal(O) hexacarbonyl [2,4]. This is rather a slow reaction and requires a large energy for the substitution to take place. Similarly, reactions with other diimine ligands have been carried out by refluxing a mixture of $M(CO)_6$ and the appropriate diimine ligand in an inert solvent such as heptane or toluene. Displacement of carbonyl ligands can also be facilitated by heating in a sealed

tube, ultraviolet light or by addition of a catalyst such as sodium borohydride [5,6].



Scheme 1

The treatment of metal(O) hexacarbonyl with chelating phosphines in the presence of trimethylamine N-oxide under mild conditions, also gives *cis*- $[M(CO)_4L_2]$ (M = Cr, Mo, W; $LS = dppm$ [bis(diphenylphosphino)methane] or $dpppp$ [1,3-bis(diphenylphosphino)propane] [7].

Results and Discussion

The crystal structures of $[Mo(CO)_4apmi]$ and $[Mo(CO)_4bpmi]$ were studied to determine the structure and geometry of these compounds. Both the compounds have distorted octahedral arrangements of ligands around the central metal atom. The Mo-C bond lengths of the two *cis* carbonyl groups in these

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complexes are shorter than those of the other two trans carbonyls since nitrogen donor ligand is known to be a poorer π -acceptor than the carbonyl ligands.

Experimental

General Method

The compounds were prepared by refluxing cis -[M(CO)₄(pip)₂] with the diimine ligand components (i.e. 2-acetyl pyridine or 2-benzyl pyridine and the appropriate amine) in stoichiometric quantities in *i*-PrOH. Dark violet crystalline solids were obtained when the mixtures were left overnight at room temperature in *i*-PrOH or on evaporation to dryness. Addition of diethyl ether to dichloromethane solution of the compounds also precipitated the dark violet solids. The product generally recrystallised in toluene,

Preparation of cis -[Mo(CO)₄(ampi)]

cis -[Mo(CO)₄(pip)₂] (2 g, 5.3mmol), 2-acetylpyridine (1cm³, 5.3mmol) and methylamine (1cm³) were introduced in *i*-PrOH (25 cm) to give cis -[Mo(CO)₄(ampi)] (0.92 g, 50% based on Mo). (Found: C, 41.9; H, 2.7; N, 8.1. C₁₂H₁₀MoN₂O₄ requires C, 41.9; H, 2.9; N, 8.1 %). This complex was characterised by ¹H NMR, IR and FAB-MS spectroscopy.

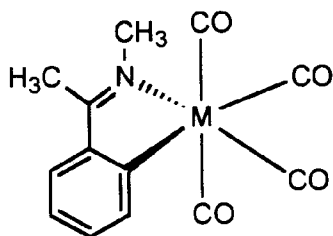


Fig. 1 [Mo(CO)₄(ampi)]

Preparation of cis -[Mo(CO)₄(bpmi)]

cis -[Mo(CO)₄(pip)₂] (1.13 g, 3 mmol), 2-benzoylpyridine (0.55 g, 3mmol) and methyl amine

(1cm³) were introduced in *i*-PrOH(25 cm³) to give cis -Mo(CO)₄(bpmi) (0.67 g, 55% based on Mo). (Found: C, 50.9; H, 3.0; N, 6.9%). It was characterized by ¹H NMR, IR and FAB' MS spectroscopy

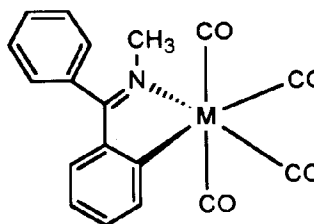


Fig. 2 [Mo(CO)₄(bpmi)]

The ¹H NMR spectra of the compounds show different resonances for methyl groups (Table 1). The singlet for methyl group bonded to carbon appears between 6 2.32 - 2.80 ppm for the compound [Mo(CO)₄(apmi)], the methyl group bonded to nitrogen shows a singlet at 6 4.02. Both ligands have multiplets in the aromatic region of the spectra between 5 6.70 and 9.32.

The IR spectra of these compounds show four absorption bands in the carbonyl region 1810 to 2020 cm⁻¹. The N=C stretching frequency is observed in the range of 1620 - 1580 cm⁻¹. The FAB mass spectra indicate the presence of parent ions and fragmentation patterns due to loss of the carbonyl ligands and imines.

X-Ray Structural Studies of Allyl Complexes

The crystal structure of the compounds [Mo(CO)₄(apmi)] and [Mo(CO)₄(bpmi)] have been determined. The molecular structures of the compounds Apmi and Bpmi are shown -in figures 3 and 4 respectively.

Selected bond distances and angles of Apmi and Bpmi are given in Tables 2 and 3 respectively. Both compounds have a distorted octahedral

Table-1: Spectroscopic Data

Complex	¹ H-NMR R1-and R	Aromatic proton	IR ν (CO), cm ⁻¹	FAB-MS [MH] ⁺	Fragmentation
cis -Mo(CO) ₄ (amp)	2.47(s, C-CH ₃), 3. N-CH ₃	7.40-9.10 (m)	2015, 1895, 1852, 1820	344	[MH-CO] ⁺ 316; [MH-4CO] ⁺ 232
cis -[Mo(CO) ₄ (bpr)]	3.47 (s, CH ₃)	7.23-9.16 (m)	2020, 1910, 1865, 1825	406	[MH-CO] ⁺ 378; [MH-4CO] ⁺ 294

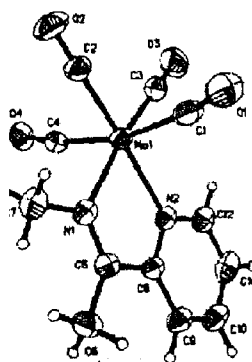
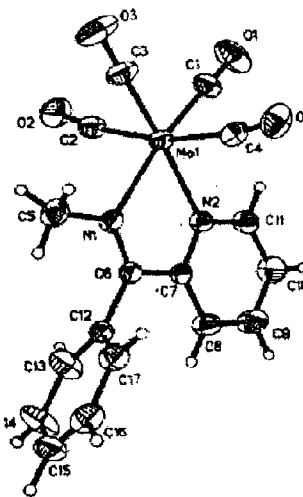
Table-2: Selected bond lengths and angles of [Mo(CO)₄(ampi)]

Bond Lengths	Å	Bond Angles	[°]
Mo-C(1)	2.056(5)	C(2)-Mo-C(3)	89.2(2)
Mo-C(2)	1.945(5)	C(2)-Mo-C(4)	82.6(2)
Mo-C(3)	1.958(5)	C(3)-Mo-C(4)	86.5(2)
Mo-C(4)	2.202(5)	C(2)-Mo-C(1)	83.5(2)
Mo-N(1)	2.235(4)	C(3)-Mo-C(1)	87.8(2)
Mo-N(2)	2.242(3)	C(4)-Mo-C(1)	166.8(2)
N(1)-C(5)	1.289(5)	C(3)-Mo-N(1)	169.5(2)
N(1)-C(7)	1.469(5)	C(2)-Mo-N(2)	172.1(2)
C(1)-O(1)	1.127(6)	O(2)-C(2)-Mo	178.2(5)
C(2)-O(1)	1.151(6)	N(1)-Mo-N(2)	71.59(13)
C(3)-O(3)	1.153(6)	O(1)-C(1)-Mo	171.1(5)
C(4)-O(4)	1.142(5)	C(5)-N(1)-C(7)	119.2(4)

Table-3: Selected bond lengths and angles of [Mo(CO)₄(bpmi)]

Bond Lengths	Å	Bond Angles	[°]
Mo-C(1)	1.950	C(1)-Mo-C(2)	85.06(14)
Mo-C(2)	2.025(4)	C(1)-Mo-C(3)	90.4(2)
Mo-C(3)	1.945(4)	C(2)-Mo-C(3)	83.84(8)
Mo-C(4)	2.051(3)	C(2)-Mo-C(4)	166.63(13)
Mo-N(1)	2.228(2)	C(3)-Mo-C(4)	84.45(13)
Mo-N(2)	2.241(2)	C(1)-Mo-N(1)	168.61(12)
C(3)-O(3)	1.161(4)	C(2)-Mo-N(1)	93.39(12)
C(4)-O(4)	1.142(4)	O(1)-C(1)-Mo	176.1(3)
N(1)-C(5)	1.476(4)	O(2)-C(2)-Mo	170.9(3)
N(1)-C(6)	1.283(4)	C(5)-N(1)-C(6)	120.0(3)
N(2)-C(7)	1.361(3)	C(4)-Mo-C(1)	88.57(13)
N(2)-C(11)	1.337(4)	C(4)-Mo-N(2)	91.77(10)
C(1)-O(1)	1.154(4)	C(3)-Mo-N(2)	171.41(12)
C(2)-O(2)	1.141(4)	N(1)-Mo-N(2)	71.91(8)

arrangement of nitrogen donor ligands around the central molybdenum atom. The Mo-C bond lengths of the two *cis* carbonyl groups in Apmi and Bpmi are shorter than those of the other *trans* carbonyls Apmi and Bpmi since nitrogen donor ligand is known to be poorer π -acceptor than the carbonyl ligands. The axial Mo-CO groups are significantly nonlinear, with the oxygen atom bent away from the diimine ligand.

Fig 3 Molecular Structure of [Mo(CO)₄(ampi)]Fig 4 Molecular structure of [Mo(CO)₄(bpmi)]

Conclusions

The structures of Apmi and Bpmi were confirmed by a single crystal X-ray diffraction studies which showed a distorted octahedral arrangement of carbonyl ligands around the metal atom. All the compounds isolated were characterized by ¹H NMR, IR and FAB-MS spectroscopy. The compounds are stable at room temperature and give strong violet coloured solutions in chloroform.

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