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The Molecular Structure of a Complex of a 2,6-Diimino–Pyridine as a Bidentate Ligand with Molybdenum Carbonyl

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Abstract

Reaction of the pyridyl–diimine ligand, 2,6-[1-(2,2-dimethylpropanimino)ethyl]pyridine (1) with $Mo(CO)_6$ has unexpectedly yielded $[Mo(CO)_4 1]$, in which the normally tridentate ligand, even under forcing conditions, is bidentate. A single crystal X-ray structure determination reveals the distorted octahedral molecule with the Mo–C distances *trans* to the nitrogen donor atoms 0.1 Å shorter than the other two Mo–C distances. Other bond lengths suggest delocalization of charge in the chelate ring and this is reinforced by proton NMR data which suggests electron flow from the metal into the pyridine ring.

Introduction

Very recently, some pyridyl–diimine ligands have been utilized to prepare various transition metal complexes with interesting properties [1–3]. All of these ligands have been found to behave as tridentate ligands coordinating by all three nitrogen atoms to the metal center. However, complexation of 2,6-diimino–pyridines with molybdenum has not been reported. In this paper we describe the synthesis, characterization, and molecular structure of a product of the reaction of 2,6-[1-(2,2-dimethylpropanimino)-ethyl] pyridine (1) with molybdenum hexacarbonyl. Here the diimino–pyridine acts as a bidentate ligand using only two of the three nitrogen atoms in the molecule to replace two carbonyl groups from the hexacarbonyl complex.

Experimental

Preparation of the Ligand

Under N_2 atmosphere a solution of neopentylamine (3.486 g, 0.040 mol) in 30 ml of benzene was added to a solution of 2,6-diacetylpyridine (3.264 g, 0.020 mol) in 50 ml of benzene. The solution was heated under reflux for 10 h. During refluxing, the water produced was separated with a trap, and the solution changed from colorless to yellow. After removal of benzene to a volume of *ca.* 10 ml, 50 ml of cyclohexane was added, producing a brown precipitate. Filtration of the precipitate gave 5.35 g of the desired product. Yield = 85%. Microanalysis of the ligand was performed by Galbraith Laboratories, Inc., Knoxville, Tenn. *Anal.* For this ligand, $C_{19}H_{31}N_3$, Calc.: C, 75.75; H, 10.30; N, 13.95. Found: C, 75.17; H, 9.70; N, 13.62%. The mass spectrum of the ligand gives the parent peak at m/e = 301 corresponding to the molecular mass of the ligand. Proton NMR data of this ligand are given in Table I.

TABLE I. Proton NMR Data (ppm) for the Free Ligand and the Complex[a] (see Scheme 1)

Compound	Ha	Hb	Hc	Hd	He
Free ligand	1.04	2.38	3.24	7.69	8.17
	(s, 18H)	(s, 6H)	(s, 4H)	(t, 1H)	(d, 2H)
Molybdenum complex	1.03	2.37	3.38		
	(s, 9H)	(s, 3H)	(s, 2H)		
	Δδ0.01	Δδ0.01	Δδ0.14	7.04	7.96
	1.15	2.46	4.17	(m, 1H)	(m, 2H)
	(s, 9H)	(s, 3H)	(s, 2H)	Δδ −0.65	Δδ −0.21
	Δδ0.11	Δδ0.08	Δδ0.79		

[a]The first set of values for Ha, Hb and Hc are for the protons on the free side chain, the second set of values are for the coordinated side chain. [b]Δδ = (chemical shift of the protons in the complex) – (chemical shift of the same protons in the free ligand).

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Preparation of the Complex

Under N_2 atmosphere, a mixture of the ligand (0.301 g, 1.00 mmol) and $Mo(CO)_6$ (1.00 mmol, 0.264 g) in 70 ml of degassed (with N_2) benzene was heated under reflux with stirring for 12 h. Removal of the solvent gave *ca.* 0.3 g of brown powder product. The product was recrystallized from cyclohexane/methanol by very slow evaporation over two weeks with a very small stream of N_2, forming some red crystals suitable for X-ray diffraction. The IR spectrum of the complex in KBr shows four bands for ν(CO) vibrations: 1985(m), 1902(vs), 1879(sh) and 1830(s) cm^{-1}. This is typical of a spectrum for a disubstituted *cis*-$Mo(CO)_4LL$ [4]. The proton NMR spectrum of the complex gave informative resonances (see Table I and the 'Discussion'.)

Structure Determination of the Complex (Fig. 1)

Molecular formula, $C_{23}H_{31}N_3O_4Mo$, $M_r = 509.46$, orthorhombic, $a = 16.625(6)$, $b = 17.185(3)$, $c = 17.438(3)$ Å, $Z = 8$, $D_m = 1.520$ g/cm, $F(000) = 2384$, space group, *Pbca*. Mo Kα radiation, $\lambda = 0.71073$ Å, $\mu = 5.474$ cm^{-1}, equivalent positions, x,y,z; $½ + x$, $1.2 - y$, $-z$; $-x$, $½ + y$, $½ - z$; $½ - x$, $-y$, $½ + z$. Diffraction experiments were performed on an Enraf-Nonius CAD-4 diffractometer [5].

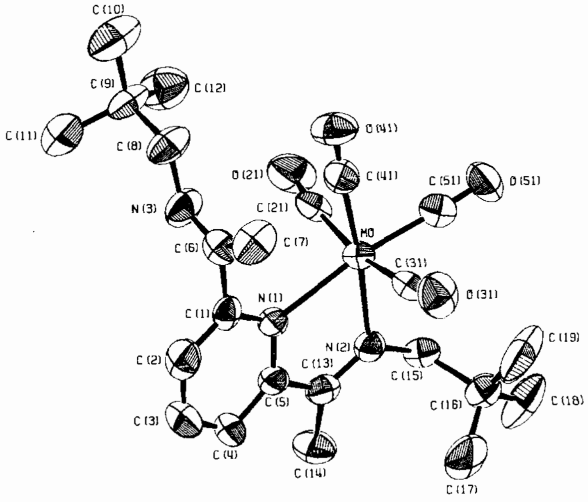
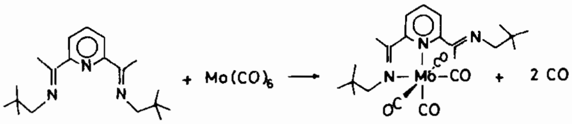


Fig. 1. Molecular structure of 2,6[1-(2,2-dimethylpropanimino)ethyl]pyridine tetracarbonyl molybdenum.

Results and Discussion

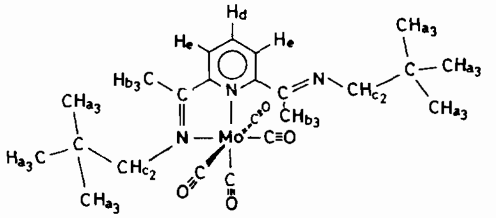
According to the molecular structure of the product, the ligand, 2,6-[1-(2,2-dimethylpropanimino)ethyl]pyridine, behaves as a bidentate ligand to displace two carbonyl groups, and one imine nitrogen remains free when the ligand reacts with $Mo(CO)_6$.



This markedly contrasts with similar ligands [1, 2] when they react with other metals, for example with $[Cu(MeCN)_4][ClO_4]$ or $[Pd(MeCN)_2Cl_2]$. In these cases these ligands act in a tridentate manner. Furthermore the bidentate coordination with Mo(0) demonstrates the difficulty of substitution of the third carbonyl in $[Mo(CO)_4LL]$ by the second imine nitrogen. Even at higher temperatures, such as that of refluxing toluene, the second imine nitrogen is unable to displace a third carbonyl. The explanation does not appear to involve a steric effect, since such ligands behave as tridentates toward smaller metal centers.

The effect of complexation upon chemical shifts of hydrogen atoms in this molecule is informative. The attachment of the molybdenum tetracarbonyl shifts the resonances of three aromatic hydrogen atoms toward higher field, and shifts the resonances of the other hydrogen atoms in the molecule toward lower field. Electron density flows via the sigma bonds from the pyridine to the Mo, but pi electron density flows from Mo into the pyridine pi system. Perhaps this is the origin of the observed (Table I, Scheme 1) upfield shift (shielding) effect on the pyridine protons in the complex. On the other hand, the molybdenum tetracarbonyl appears to withdraw electron density from the two side chains resulting in downfield shifts of resonances of the protons in the two side chains. In particular, the chemical shift of the two methylene protons in the non-coordinated side chain is unexpectedly large ($\Delta\delta = 0.14$ ppm), suggesting that the molybdenum tetracarbonyl in the complex exhibits a remote effect upon the proton resonance probably via the double bond system rather than through space. If the interaction were through space it would be expected that the methyl protons would have experienced a greater shift than they do.

The molecular structure of the complex obtained by single crystal X-ray diffraction analysis indicates that the complex has a distorted octahedral structure. As expected, the two carbonyls which are *trans* to



Scheme 1. The complex with labeled hydrogen atoms for assignment of proton NMR resonances.

TABLE II. Selected Bond Distances (Å) and Angles (°) for the Complex

Mo–N(1)	2.289(7)	Mo–N(2)	2.270(7)
Mo–C(21)	2.041(10)	C(21)–O(21)	1.143(12)
Mo–C(31)	2.031(10)	C(31)–O(31)	1.144(13)
Mo–C(41)	1.948(10)	C(41)–O(41)	1.166(12)
Mo–C(51)	1.938(10)	C(51)–O(51)	1.165(12)
N(1)–C(1)	1.342(12)	N(1)–C(5)	1.374(10)
C(1)–C(6)	1.515(13)	C(5)–C(13)	1.466(13)
C(6)–N(3)	1.240(12)	C(13)–N(2)	1.295(12)
C(21)–Mo–C(31)	168.5(3)	C(31)–Mo–C(41)	86.6(4)
C(21)–Mo–C(41)	85.1(4)	C(31)–Mo–C(51)	88.1(4)
C(21)–Mo–C(51)	86.0(4)	C(41)–Mo–C(51)	84.9(4)
N(1)–Mo–C(21)	96.4(3)	N(2)–Mo–C(21)	91.8(3)
N(1)–Mo–C(31)	90.9(3)	N(2)–Mo–C(31)	98.8(3)
N(1)–Mo–C(41)	103.6(3)	N(2)–Mo–C(41)	174.8(3)
N(1)–Mo–C(51)	171.3(3)	N(2)–Mo–C(51)	99.1(3)
N(1)–Mo–N(2)	72.5(2)		
Mo–N(1)–C(5)	114.2(6)		
Mo–N(2)–C(13)	117.9(6)		
N(1)–C(5)–C(13)	117.3(7)		
C(5)–C(13)–N(2)	117.1(8)		

TABLE III. Non-hydrogen Atomic Coordinates (× 10)[a]

Atom	*x*	*y*	*z*
Mo	1603.0(4)	1230.3(4)	1221.7(4)
N(1)	503(4)	451(4)	1407(4)
N(2)	1785(4)	138(4)	511(4)
N(3)	-636(5)	1840(5)	1891(4)
C(1)	-119(6)	572(5)	1884(5)
C(2)	-697(6)	26(7)	2008(6)
C(3)	-665(7)	-693(6)	1651(7)
C(4)	-34(6)	-824(5)	1154(6)
C(5)	536(6)	-248(5)	1026(5)
C(6)	-228(6)	1362(5)	2255(5)
C(7)	113(10)	1409(8)	3066(7)
C(8)	-844(7)	2587(5)	2259(6)
C(9)	-1273(7)	3115(6)	1701(6)
C(10)	-1468(8)	3883(6)	2104(7)
C(11)	-2064(8)	2741(6)	1422(8)
C(12)	-749(8)	3270(7)	1002(7)
C(13)	1024(6)	-364(5)	489(5)
C(14)	1143(9)	-1044(6)	-52(8)
C(15)	2481(5)	52(5)	-2(5)
C(16)	3196(6)	-419(5)	330(5)
C(17)	2930(8)	-1200(7)	623(9)
C(18)	3764(7)	-553(8)	-343(7)
C(19)	3609(8)	5(9)	943(8)
C(21)	1156(5)	1822(5)	301(5)
C(31)	2095(5)	856(5)	2222(5)
C(41)	1347(5)	2168(5)	1800(5)
C(51)	2612(5)	1749(5)	1002(5)
O(21)	953(5)	222(4)	-188(4)
O(31)	2392(4)	737(4)	2802(4)
O(41)	1233(4)	2738(4)	2148(4)
O(51)	3216(4)	2027(4)	884(4)

[a] e.s.d.s in parentheses.

the two nitrogen donor atoms have shorter M–C distances (by roughly 0.1 Å) than the other two carbonyls. The C=N double bond length in the coordinated side chain is longer than the non-coordinated C=N bond length by 0.05 Å, again as expected. (See Table II. The coordinates of non-hydrogen atoms of the molecule are given in Table III.) The shortening of C(5)–C(13) (by 0.05 Å), which is paralleled by the lengthening of C(13)–N(2) (by 0.05 Å) suggests that there is some delocalization of charge in the chelate ring.

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