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Syntheses and Structure of Molybdenum(0) Dimers Based on Tetracyanobiimidazole

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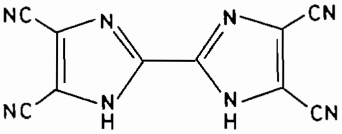
In a recent preliminary communication [1] we reported the synthesis and properties of a novel new compound 4,4',5,5'-tetracyano-2,2'-biimidazole (H_2Tcbiim).



As we anticipated, the strongly electron withdrawing cyano substituents profoundly alter the electronic structure compared to the parent biimidazole system we investigated earlier [2, 3, 4]. The H_2Tcbiim system is far more acidic and always forms complexes as the dianion. It retains the potential for forming aromatic bridges between pairs of metal ions however, and interactions between such linked metal centers has been of increased interest lately, especially in the context of intermolecular redox reactions. H_2Tcbiim reacts readily with metals in low oxidation states to yield binuclear complexes and we have described the syntheses and reactions of Rh(I) and Ir(I) species elsewhere [5]. We have also demonstrated the bridging of Cu(I) ions by Tcbiim^{2-} and we are investigating this system further [6]. Beck and coworkers were able to form dimers of zero-valent molybdenum using biimidazole [7] and we report here some analogous compounds based on H_2Tcbiim. The unique properties of the percyano substituted imidazole make these compounds easier to prepare and somewhat more tractable.

Reaction of the sodium salt of Tcbiim^{2-} (1 mmol) with $Mo(CO)_6$ (2 mmols) in 25 ml of diglyme for four hours at 60 C under N_2 produced an orange solution. Addition of the stoichiometric amount of Ph_4AsCl in 20 ml ethanol, stripping the solvents and extraction with CH_2Cl_2 yields a yellow solution from which the yellow microcrystalline compound $[Ph_4As]_2[(CO)_4Mo(Tcbiim)Mo(CO)_4]$ can be isolated by evaporation under vacuum. The IR spectrum of the complex shows the nitrile band of the ligand at 2243 cm^{-1} and four carbonyl peaks at 2017, 1899, 1864, and 1828 cm^{-1} corresponding to the C_{2v} local symmetry. The complex $[Et_4N]_2$-$[(CO)_3(PPh_3)Mo(Tcbiim)Mo(PPh_3)(CO)_3]\cdot CH_3CN$ is prepared by stirring at room temperature 1 mmol of $(Et_4N)_2$Tcbiim and 2 mmol of *fac*-$Mo(CH_3CN)_3(CO)_3$ in 20 ml of dry acetonitrile for two hours. Addition of 2 mmol of triphenylphosphine, further stirring at 60 C and reduction of the volume, leads to precipitation of the yellow microcrystalline product. The IR spectrum shows a nitrile band at 2230 cm^{-1} and three carbonyl stretches at 1900, 1786, and 1761 cm^{-1}. Crystals of this compound suitable for x-ray diffraction were grown by diffusion of ether into an acetonitrile solution. Crystal data: $Mo_2P_2O_6N_{11}C_{70}H_{73}$; space group $P2_1/n$; a = 11.241(3) Å, b = 27.350(13) Å, c = 12.350(6) Å; β = 103.01(3); V = 3699(2) Å^3; Z = 2. Refinement of 3770 observed reflections led to a final R = 4.9%. Details of data collection and procedures and programs used have been described previously [8].

TABLE I. Selected Bond Distances (Å). E.s.d. in Parenthesis.

Mo	C41	1.929(7)
Mo	C51	1.932(7)
Mo	C61	1.961(7)
Mo	Ni	2.316(5)
Mo	N3	2.316(5)
Mo	P	2.563(2)
P	C31	1.818(7)
P	C21	1.848(7)
P	C11	1.854(6)
C41	O41	1.171(8)
C51	O51	1.168(7)
C61	O61	1.158(8)
N1	C2	1.330(7)
N1	C5	1.380(7)
C2	N3	1.343(7)
C2	C2	1.427(11)
N3	C4	1.359(7)
C4	C5	1.403(9)
C4	C6	1.425(9)
C5	C7	1.407(9)
C6	N4	1.124(8)
C7	N5	1.150(8)

The structure with atom labels is shown in Fig. 1. Selected bond distances and angles are given in Tables I and II. The complex anion is centrosymmetric with an inversion center located between the two equiva-

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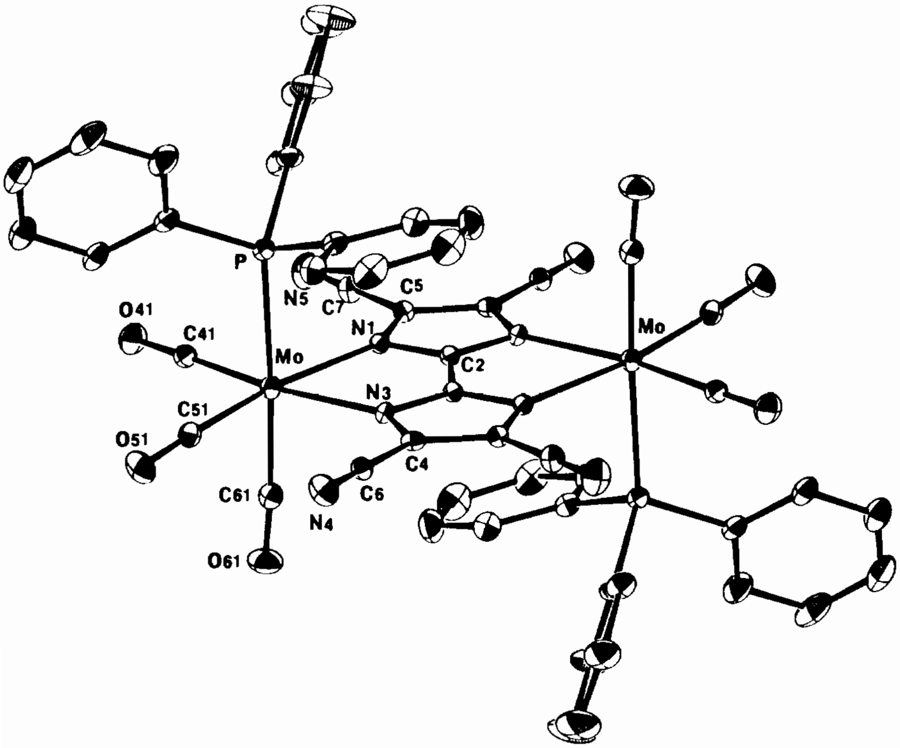

Fig. 1. Representation of structure.

TABLE II. Selected Angles (°). E.s.d. in Parenthesis.

C41	Mo	C51	89.01(28)
C41	Mo	C61	88.64(28)
C41	Mo	N1	97.78(22)
C41	Mo	P	91.56(20)
C51	Mo	C61	83.65(27)
C51	Mo	N3	98.51(23)
C51	Mo	P	92.25(20)
C61	Mo	N1	93.05(22)
C61	Mo	N3	94.28(23)
N1	Mo	P	90.98(13)
N3	Mo	P	86.04(13)
N1	Mo	N3	79.84(17)
041	C41	Mo	178.48(95)
051	C51	Mo	176.11(68)
061	C61	Mo	175.44(63)
C2	N1	C5	102.38(47)
C2	N1	Mo	111.34(36)
C5	N1	Mo	146.16(41)
N1	C2	N3	117.45(49)
N1	C2	C2′	121.65(67)
N3	C2	C2′	120.87(69)
C2	N3	C4	102.60(49)
C2	N3	Mo	111.24(36)
C4	N3	Mo	146.16(42)
N3	C4	C5	109.12(51)
N3	C4	C6	123.28(59)
C5	C4	C6	127.60(56)
N1	C5	C7	123.10(56)
C4	C5	C7	128.46(56)
N4	C6	C4	177.41(74)
N5	C7	C5	178.9(13)

lent C2 atoms. The biggest distortion from regular octahedral geometry at the metal is the N1–Mo–N3 angle of 79.8. Similar values for this angle have been found in other structures containing Tcbiim^{2-} [9]. Although not required by the space group, the two Mo–N bond lengths are identical and except for the phenyl rings the ion has near C_{2h} symmetry. The Mo–Mo distance across the bridge is 5.96 Å. The tetracyanobiimidazole bridge is planar with negligible deviation, and the molybdenum and equatorial carbonyls lie within ±0.5 Å of this plane. The Mo–C41 and Mo–C42 are only 0.03 Å shorter than Mo–C61 which is trans to the phosphine. This indicates that the tetracyanobiimidazole dianion is nearly as effective a pi acceptor as the phosphine. This is further corroborated by the CO stretching frequencies in the carbonyl anion which average 20 cm^{-1} higher than those of corresponding unsubstituted biimidazole complex [7]. Thus tetracyanobiimidazole can be expected to readily bridge low valent metals and to form the basis for a wide variety of organometallic dimers. Furthermore, its greater acidity and solubility make synthetic procedures somewhat simpler compared to the parent biimidazole compound. The synthesis of the phosphine derivative described above takes place by the stepwise substitution of the easily displaced acetonitriles. This procedure can be used to prepare a variety of substituted dimers bridged by tetracyanobiimidazole. We are currently investigating the preparation and reactivity of this class of compounds.

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9 In a dimeric complex of Cu(I) we have recently studied by x-ray diffraction the comparable angle was 81.59°. (Unpublished result)