
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 (H₂Tcbiim).

As we anticipated, the strongly electron withdrawing cyan0 substituents profoundly alter the electronic structure compared to the parent biimidazole system we investigated earlier [2, 3, 4]. The H₂Tcbiim 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. H₂Tcbiim 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 Tcbiim⁵⁻ and we are investigating this system further [6]. Beck and co-workers were able to form dimers of zero-valent molybdenum using biimidazole [7] and we report here some analogous compounds based on H₂Tcbiim. 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⁻ (1 mmol) with Mo(CO)₆ (2 mmols) in 25 ml of diglyme for four hours at 60 C under N₂ produced an orange solution. Addition of the stoichiometric amount of Ph₄AsCl in 20 ml ethanol, stripping the solvents and extraction with CH₂Cl₂ yields a yellow solution from which the yellow microcrystalline compound [Ph₄As]₂[CO₄Mo(Tcbiim)Mo(CO)₆] 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 1701, 1848, and 1828 cm⁻¹ corresponding to the Cᵥ local symmetry. The complex [Et₄N]₂[(CO₃)₂PPh₃]Mo(Tcbiim)Mo(PPh₃)(CO)₆]·CH₃CN is prepared by stirring at room temperature 1 mmol of (Et₄N)₂Tcbiim and 2 mmol of sec-Mo(CI₃CN)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: Mo₂P₂O₄N₂C₇0H₇₂; space group P2₁/n; a = 11.241(3) Å, b = 27.350(13) Å, c = 12.350(6) Å; β = 103.01(3); V = 3699(2) Å³; 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.

|     | C41 | 1.929(7) |
|     | C51 | 1.932(7) |
|     | C61 | 1.961(7) |
| Mo  | N1  | 2.316(5) |
| Mo  | N3  | 2.316(5) |
| Mo  | P   | 2.563(2) |
| P   | C31 | 1.818(7) |
| P   | C21 | 1.848(7) |
| 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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**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) |
| C61 | Mo  | P   | 90.98(13) |
| N1  | Mo  | N3  | 79.04(17) |
| N3  | Mo  | P   | 86.04(13) |
| N1  | Mo  | N3  | 79.04(17) |
| O41 | C41 | Mo  | 178.48(95) |
| O51 | C51 | Mo  | 176.11(68) |
| O61 | 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  | 173.10(56) |
| C4  | C5  | C7  | 128.46(56) |
| N4  | C5  | C4  | 177.41(74) |
| N5  | C7  | C5  | 176.9(12) |

![Fig. 1. Representation of structure.](image)

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 Tchim^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 C2v symmetry. The Mo-Mo distance across the bridge is 5.96 Å. The tetracyanobimidazole 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 tetracyanobimidazole 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 bimidazole complex [7]. Thus tetracyanobimidazolate 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 bimidazole 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 tetracyanobimidazole. We are currently investigating the preparation and reactivity of this class of compounds.
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References

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