

**Figure 1.** Chiral recognition between the *S* enantiomers of **1** and **2**. Three bonding interactions are shown: a van der Waals ( $\pi$ - $\pi$ ) interaction between the dinitrobenzoyl ring of **2** and the naphthyl ring of **1**, a hydrogen bond between the dinitrobenzamide proton of **2** and the carbonyl of **1**, and a second hydrogen bond between the amino proton of **1** and the C-terminal carbonyl of **2**.

obtained in the same experiment. When the target resonance is a multiplet, selective population-transfer suppression techniques were used.<sup>3</sup> A fairly large number of intermolecular NOEs are seen in the *S*-*S* mixture, indicating that, at the concentrations used, a large proportion of the material is present as the stable *S*-*S* complex and that this complex has a well-defined structure. Although the intermolecular enhancements are modest, they are reproducible and specific.<sup>4</sup> In contrast, only one intermolecular NOE was observed in the less stable *R*-*S* mixture.

The largest intermolecular effects are seen in the *S*-*S* complex for the aromatic ring protons of **1** and **2**. These protons normally have but inefficient relaxation processes available to them and give the most dramatic response to external enhancements of relaxation. Upon saturation of the overlapping H13 *o*-dinitrobenzoyl ring protons and the H14 dinitrobenzamide proton resonances, intermolecular NOEs are observed at H1 (4.8%), H2 (1.8%), and H7 (3.9%) of the naphthyl ring of **1**. The complementary effect on H13 (1.8%) is seen upon saturation of H1. Saturation of para proton H12 on the dinitrobenzoyl ring gives rise to specific effects in the naphthyl ring system at H5 (3.1%) and H6 (1.9%). Irradiation of the H5 multiplet gives rise to NOE enhancement of 1.5% at H12. Because the resonances of H6 and H7 occur in a crowded portion of the spectrum, these initially tentative NOE assignments were confirmed by intramolecular NOEs observed upon irradiation of H5 and H1, respectively. The resulting unambiguous assignments allow one to conclude that the two aromatic systems in the *S*-*S* complex are quite close, as expected for a  $\pi$ -donor-acceptor system.

Furthermore, saturation of the H17 methylene protons of the C-terminal amide group of **2** causes larger intermolecular NOEs

at H2 (2.1%) than at H1 (0.5%), indicating that, on a time-average basis, H1 and H2 are near the *n*-propyl group of **2**, and the naphthyl rotamer placing H2 closest to the *n*-propyl group of **2** is preferentially populated. Additionally, intramolecular NOEs indicate that the naphthyl ring is oriented so as to place H1 syn to proton H9 on the chiral center of **1**, since saturation of the H9 resonance gives rise to a much larger effect at H1 (10.2%) than at H2 (1.9%). Saturation of amino proton resonance H8 produces NOEs at H1 (2.3%) and at H2 (5.4%). This intensity pattern suggests that H8 is anti to H9. Interestingly, saturation of H8 gives rise to a negative NOE (-9.5%) at H9, presumably because indirect NOEs from H1 and H2 predominate at H9. This also is consistent with the anti relationship of H8 and H9. For the *R*-*S* mixture, intramolecular NOEs indicate considerably less preference for the naphthyl rotamer depicted in Figure 1. Upon saturation of H9 in the *R*-*S* mixture, the H2 resonance is enhanced 4.8% as opposed to the H1 enhancement of 7.3%. Finally, saturation of the carbomethoxy proton resonance of **1** (H11), gives rise to an NOE at H13 (1.8%) of the dinitrobenzoyl ring of **2**.

In contrast, the *R*-*S* complex shows but one intermolecular NOE. An enhancement of the intensity of the signals of the dinitrobenzoyl ring protons, H13, occurs after saturation of the methoxy protons, H11, of **1**. This seems to indicate that the dinitrobenzamide N—H...O=C hydrogen bond between **1** and **2** occurs to a some extent but that the *R*-*S* complex has no strongly preferred structure.

The nuclear Overhauser effects noted here provide direct support for the initially proposed chiral recognition model. Such studies can be expected to become essential tests of the validity of future chiral recognition models. However, *intermolecular NOEs* have a vast potential for the structural elucidation of a variety of low molecular weight solution complexes in general and are not restricted to the study of chiral recognition mechanisms.

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**Supplementary Material Available:** Complete tabulation of <sup>1</sup>H chemical shifts, <sup>1</sup>H *T*<sub>1</sub> values, and intra- and intermolecular NOE data for both the *R*-*S* and *S*-*S* complex (5 pages). Ordering information is given on any current masthead page.

## Decarbonylation of Molybdenum(II) Carbonyl Complexes: A New Route to Quadruply Bonded Molybdenum(II) Dimers

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Multiple metal-metal bonds are now well established and, among them, the quadruple bond between molybdenum(II) atoms has perhaps been the most intensively studied.<sup>1</sup> Despite this, most of the known Mo<sub>2</sub><sup>4+</sup> derivatives are still prepared via ligand-exchange reaction starting from the molybdenum(II) acetate, its preparation from Mo(CO)<sub>6</sub> being the most important route to the formation of the Mo<sub>2</sub><sup>4+</sup> core. Other synthetic routes to Mo<sub>2</sub><sup>4+</sup> species from mononuclear precursors generally involve reduction of higher oxidation state compounds, such as MoX<sub>3</sub> (X = Cl, Br),<sup>2</sup> MoCl<sub>4</sub>,<sup>3</sup> MoH<sub>4</sub>(PMePh<sub>2</sub>)<sub>4</sub>,<sup>4</sup> and MoO<sub>3</sub>.<sup>5</sup> Only one example seems

(4) The magnetization of spin-<sup>1</sup>/<sub>2</sub> nuclei on molecules involved in fast-exchange complex formation has been described by Bothner-By and co-workers using the equation

$$m_i = \frac{fT_c m_f + cT_f m_c}{fT_c + cT_f}$$

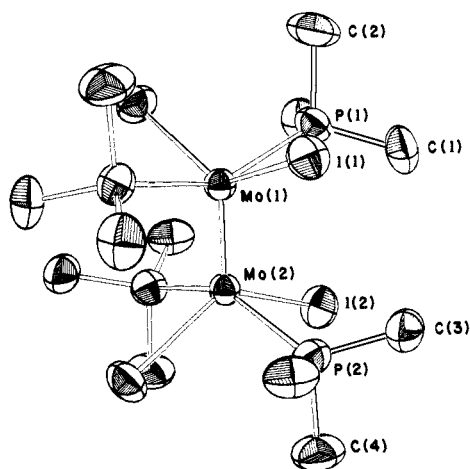
where *m*<sub>i</sub> is the observed magnetization, *m*<sub>f</sub> and *m*<sub>c</sub> are the equilibrium magnetizations free and complexed, respectively, of the observed nucleus, *f* and *c* are the mole fractions of free and complexed forms of the molecule on which the observed nucleus resides, and *T*<sub>f</sub><sup>-1</sup> and *T*<sub>c</sub><sup>-1</sup> are the rates of approach to equilibrium magnetization of the observed nucleus in the free and complexed forms, respectively. Balaram, P.; Bothner-By, A. A.; Breslow, E. *Biochemistry* 1973, 12, 4695. Further studies of complexation between the *S* enantiomers of **1** and **2** indicate that at the concentrations used for this study, approximately 60% of each component is complexed at equilibrium. On the basis of the above equation, then, NOEs observed should be about 60% of the intensity expected for complete complexation between **1** and **2**. A more detailed description of these studies is in preparation. For further discussion of NOE in exchanging systems, see: Borzo, M.; Maciel, G. E. *J. Magn. Reson.* 1981, 43, 175.

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**Figure 1.** ORTEP diagram of  $\text{Mo}_2\text{I}_4(\text{PMe}_3)_4$  in compound **5** with the atomic numbering scheme employed. Distances: Mo1–Mo2, 2.129 (1); Mo1–I1, 2.762 (1); Mo1–P1, 2.566 (2); Mo2–I2, 2.756 (1); Mo2–P2, 2.557 (2); P1–C1, 1.839 (5); P1–C2, 1.883 (8); P2–C3, 1.835 (5); P2–C4, 1.896 (8) Å. Angles: Mo2–Mo1–I1, 113.63 (2)°; Mo2–Mo1–P1, 104.39 (5)°; I1–Mo1–I1', 132.74 (3)°; I1–Mo1–P1, 84.28 (2)°; P1–Mo1–P1', 151.23 (9)°; Mo1–Mo2–I2, 113.83 (2)°; Mo1–Mo2–P2, 104.70 (4)°; I2–Mo2–I2', 132.35 (3)°; I2–Mo2–P2, 84.12 (2)°; P2–Mo2–P2', 150.60 (9)°.

to have appeared in the literature of a  $\text{Mo}_2^{4+}$  species having been prepared from a Mo(II) non-metal–metal-bonded starting material, i.e.,  $\text{Mo}_2\text{L}_2$  (L = porphyrin) from the corresponding mononuclear complex  $\text{MoL}(\text{PhC}\equiv\text{CPh})$ .<sup>6</sup> It is also to be noted that CO and other strong  $\pi$ -acidic ligands are generally found to destabilize M–M multiple bonds.<sup>1</sup> For these reasons, we consider it unusually interesting that dimolybdenum(II) species of the  $\text{Mo}_2\text{I}_4\text{L}_4$  and  $\text{Mo}_2\text{I}_4(\text{L-L})_2$  type [L =  $\text{PMe}_3$  (**1**); L–L = dpmm (**2**)] can be prepared directly from Mo(II) carbonyl iodide starting materials;  $\text{Mo}_2\text{I}_4(\text{CO})_8$ ,<sup>7</sup> **3**, now easily available in large amounts,<sup>8</sup> was the system of our choice.

This synthetic method has other points of interest: it is a simple and direct route to dinuclear Mo(II) iodides, otherwise obtained by the longer procedure of halide exchange from the corresponding bromides,<sup>9</sup> by coordinative addition to  $\beta$ - $\text{MoI}_2$ ,<sup>10</sup> or by the recently developed<sup>11</sup> reaction of the acetate with  $\text{Me}_3\text{SiI}$  in the presence of the appropriate ligand. Furthermore, it represents the reverse process to the known<sup>12</sup> reaction of  $\text{Mo}_2\text{X}_4(\text{PR}_3)_4$  complexes with carbon monoxide, in which there is disruption of the quadruple bond and formation of mononuclear carbonyl derivatives of Mo(II) and Mo(0). Finally, it is a new pattern of reactivity for complexes of the  $\text{M}_2\text{X}_4(\text{CO})_8$  type.

Treatment of **3** with 4 equiv of  $\text{PMe}_3$  in toluene as solvent at room temperature leads to CO evolution and formation of an orange solution. Reflux (5 h) results in a change of color to deep blue. From this solution compound **1** was isolated by evaporation to dryness and recrystallization from *n*-hexane, yield 41%. It was characterized by vibrational and electronic spectroscopy, <sup>1</sup>H and <sup>31</sup>P NMR, and elemental analysis.<sup>13</sup>

An analogous reaction was carried out from  $\text{MoI}_2(\text{CO})_3\text{THF}_2$  (**4**) and 4 equiv of the phosphine in refluxing THF, the carbonyl complex having been obtained in situ by dissolving **3** in  $\text{THF}$ .<sup>8</sup>

From the final blue-green solution a blue solid,  $\text{Mo}_2\text{I}_4(\text{PMe}_3)_4\cdot 2\text{THF}$  (**5**) crystallized upon cooling to room temperature. This had the same visible spectrum as **1**: the IR spectrum (Nujol mull), on the other hand, exhibited a strong band at  $1070\text{ cm}^{-1}$  which was not present in the corresponding spectrum of **1**. We assign this band to the C–O–C vibration of lattice THF. The presence of THF was confirmed by <sup>1</sup>H NMR (broad triplets at  $\delta$  1.48 and 3.62, 1:1 relative intensity) and by a crystal structure determination,<sup>14</sup> which established the nature of the compound as **5**. A view of the dimer in compound **5** is shown in Figure 1.

Compound **1** is air-sensitive, but it resists aerial oxidation for a few hours, even in  $\text{CH}_2\text{Cl}_2$  solution. Compound **5** loses its lattice THF when pumped or exposed to air, and the crystal for X-ray analysis had therefore to be mounted under solvent.

Reaction of **3** with 2 equiv of dpmm in toluene at room temperature gave rise to an orange solution from which orange crystals soon began to form. Their analytical and spectroscopic data are in accord with their formulation as  $\text{MoI}_2(\text{CO})_3\text{dpmm}$  (**6**).<sup>15</sup> Reflux of compound **6**, either isolated or obtained in situ as previously described, for 12 h in toluene as solvent afforded crystalline  $\text{Mo}_2\text{I}_4\text{dpmm}_2\cdot 2\text{toluene}$  (**7**), identified by comparison of its vibrational and electronic spectra with those of an authentic sample<sup>11,16</sup> (yield 86%).

Compound **5** appears to be the first Mo(II) iodide of the  $\text{Mo}_2\text{I}_4\text{L}_4$  type and one of the few iodide-containing compounds of the  $\text{Mo}_2^{4+}$  core to be crystallographically characterized. The dinuclear molecule has imposed  $C_{2v}$  symmetry, the Mo–Mo vector lying along the twofold axis and the two planes passing through Mo(1), Mo(2), I(1), I(1'), P(2), and P(2') and through Mo(1), Mo(2), I(2), I(2'), P(1), and P(1'). Although it is not isostructural with  $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$ ,<sup>17</sup> the two molecules have essentially the same geometry, typical of  $\text{Mo}_2\text{X}_4\text{L}_4$  compounds. The Mo–Mo distances in compound **5** and its chlorine analogue are exactly the same, and this confirms the rule<sup>18</sup> that halogen exchange has little, if any, effect on the metal–metal bond length. The Mo–I distance [average 2.759 (1) Å] is a little shorter than those found for trans iodides in the  $[\text{Mo}_2\text{I}_6(\text{H}_2\text{O})_2]^{2-}$  anions<sup>19</sup> [average 2.790 (1) Å for both the pyridinium<sup>19a</sup> and 2-picolinium<sup>19b</sup> salts]. This may be due to the negative charge of the latter species, since the Mo–Cl and Mo–I distances in the  $\text{Mo}_2\text{X}_4(\text{PMe}_3)_4$  molecules differ by 0.345 Å, which is the accepted difference in the covalent radii of Cl and I. The Mo–P distances in **5** are virtually the same as the corresponding ones found in  $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$  [2.556 (2) vs. 2.545 (1) Å].<sup>17</sup> Further work is under way to explore the generality of this new synthetic method for molybdenum as well as tungsten dimers, with the attention also focused on the characterization of intermediate species.

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**Supplementary Material Available:** Tables of fractional atomic coordinates and temperature parameters, anisotropic temperature parameters, and bond distances and angles for **5** (3 pages); tables of observed and calculated structure factors for **5** (8 pages). Ordering information is given on any current masthead page.

(14) Crystallographic data: Orthorhombic,  $Cmcm$ ,  $a = 19.412$  (5) Å,  $b = 9.789$  (5) Å,  $c = 20.165$  (8) Å,  $Z = 4$ ,  $R = 0.033$ ,  $R_w = 0.058$ . 64 parameters were refined using 1487 reflections with  $F_o^2 > 3\sigma(F_o^2)$ . The THF molecule was found to be disordered, the two independent configurations having about half-occupancy each, and the parameters of the corresponding atoms were fixed during the last cycles of refinement.

(15) Compound **6**: Anal. Calcd for  $\text{C}_{28}\text{H}_{22}\text{I}_2\text{MoO}_3\text{P}_2$ : C, 41.1; H, 2.7. Found: C, 41.7; H, 2.9. IR (toluene) 2043 m, 1973 s, 1921 m  $\text{cm}^{-1}$ ; (Nujol mull), 3020 w, 2040 m, 1940 vs br, 1910 m, 1590 w, 1575 w, 1485 m, 1435 m, 1310 w, 1190 w, 1160 vw, 1095 s, 770 w, 740 s, 725 s, 690 s, 675 w, 575 s, 525 s, 500 m, 490 m, 470 m s, 455 m, 350 m  $\text{cm}^{-1}$ .

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(13) Compound **1**: Anal. Calcd for  $\text{C}_{12}\text{H}_8\text{I}_4\text{Mo}_2\text{P}_4$ : C, 14.4; H, 3.6%. Found: C, 14.5; H, 3.8%. IR (Nujol mull) 1420 m, 1415 sh, 1295 m, 1280 m, 1165 w, 900 s, 850 w, 730 m, 670 w, 345 w, 335 w  $\text{cm}^{-1}$ ; <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ , ppm)  $\delta$  1.76 s; <sup>31</sup>P NMR ( $\text{C}_6\text{D}_6$ , ppm from external  $\text{H}_3\text{PO}_4$ )  $\delta$  -14.98; vis ( $\text{CH}_2\text{Cl}_2$ , 25 °C) 631 ( $\epsilon$   $4.33 \times 10^3$ ), 394 ( $\epsilon$   $8.55 \times 10^3$ ) nm.