Journal of Organometallic Chemistry, 346 (1988) C19–C23
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Linked bis(μ-phosphido) and related ligands for metallic clusters

VI *. Incorporation of $(CO)_4Fe$ into complexes which contain a bis(μ-phosphido)-supported Mo≡Mo functionality to give unsaturated 46-electron Mo_2Fe clusters

Evan P. Kyba **, Michael C. Kerby, Ram P. Kashyap, Karen L. Hassett and Raymond E. Davis *

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712 (U.S.A.)

(Received November 4th, 1987)

Abstract

Reaction of [μ-1,2-phenylenebis(phenyl- or t-butyl-phosphido)-*P*,*P*](μ-carbonyl)-bis(η^5-cyclopentadienyl)dimolydenum(*Mo≡Mo*) with nonacarbonyldiiron gave 46-electron Mo_2Fe complexes, which were shown by X-ray crystallography in one case to have an open trimetalla structure (phenylphosphido), and in the other, a triangulo structure (t-butylphosphido). The open triametalla species is fluxional as a result of metal-to-metal migrations, whereas the triangulo cluster is nonfluxional.

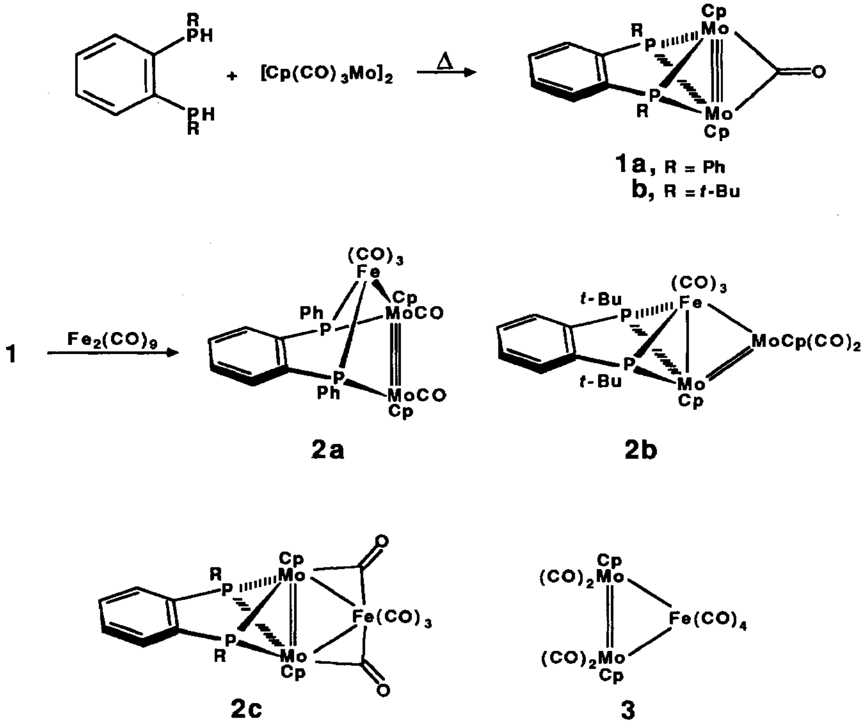
Interest in transition metal clusters has been quite intense in recent years, not only because such species represent possible conceptual bridges between homogeneous and heterogeneous catalysts [2], but also because they represent synthetic challenges [3]. Mixed metal clusters represent a further challenge since, in general, they must be prepared by appropriate staging of reactivity of at least two different metallic reactants. We envisioned the synthesis of heteronuclear clusters by the reaction of reactive transition metallic intermediates with the unsaturated MoMo bond . In this report we describe the synthesis and some of the properties of two Mo_2Fe species obtained via such a reaction utilizing tetracarbonyliron, isolobal with methylene [4].

We have described [5] the synthesis of **1a**, and **1b** was formed similarly in 60% yield (Scheme 1). These dark-green crystalline complexes are somewhat unstable in

---

* For part V see ref. 1.

** Present address: Alcon Laboratories, Inc., 6201 South Freeway, Fort Worth, Texas 76134-2099 (U.S.A.)



Scheme 1.

air in the solid state and quite unstable to air in solution. They react readily with ligands such as carbon monoxide and diphenylphosphine, as well as Brønsted acids [5].

Reaction of either **1a** or **1b** at room temperature in tetrahydrofuran with nonacarbonyldiiron resulted in the formation in 77 and 29% yields, respectively, of complexes with the composition $\mathbf{1}\cdot Fe(CO)_4$ (**2a**,**2b**). Despite the apparent close similarity of the two species, i.e., only the substituents on the μ-phosphido moieties are different, they exhibited quite different spectroscopic properties. Thus, **2a** * was fluxional at ambient temperature in CH_2Cl_2 solution, as evidenced by a broad singlet absorption in the $^{31}P\{H\}$ NMR spectrum at δ 138 ppm, whereas at $-80\,°C$ in the same solution, two somewhat broadened singlets were observed at δ 194 and 85 ppm. In contrast, **2b** ** in CH_2Cl_2 exhibited a sharp singlet at δ 165.7 ppm, which was invariant down to $-80\,°C$.

---

* **2a**; ^1H NMR ($CDCl_3$, 30 °C) δ 7.66 (m, 4 H), 7.48 (m, 6 H), 7.04 (m, 2 H), 6.92 (m, 2 H), 4.91 (s, 10 H); partial ^{13}C NMR ($CDCl_3$, 30 °C) δ 94 (s, Cp); IR (CH_2Cl_2 solution) μ(CO) 2020 (s), 1965 (s), 1865 (w), 1785 (s) cm^{-1}.

** **2b**; ^1H NMR ($CDCl_3$, 30 °C) δ 7.38 (m, 2 H), 6.63 (m, 2 H), 4.922 (s, 5 H), 4.752 (t, J 1.0 Hz, 5 H), 1.573 (br d, J 16.5 Hz, 18 H); IR (toluene solution) ν(CO) 2020 (s), 1958 (m), 1938 (m), 1817 (m), 1776 (s) cm^{-1}.

The results of X-ray structure analyses of **2a** * and **2b** * are presented as ORTEP plots in Fig. 1. With **2a**, the incorporation of the $(CO)_4Fe$ fragment has not perturbed substantially the triple bonding of the Mo_2 moiety, since D(MoMo) is 2.532 Å in **1a** [5] and 2.537 Å in **2a**. The bond distances and angles of the heavy atom core are unexceptional, although there are not many data with which to compare the Mo–Fe bond length. The two carbonyl groups on the molybdenum centers have a dihedral angle of 148°, so that substantial molecular motion is necessary upon a 1,2-shift of the Fe center, presumably contributing to a barrier to such motion sufficiently high to make it slow on the ^{31}P NMR time scale at $-80\,^{\circ}C$. It is clear that it is iron migration which makes the phosphido centers equivalent, because the Cp ligands are also rendered equivalent in the fluxional process. Such metal to metal migration of a metal center is a relatively rare phenomenon [3].

Although we had originally envisioned the reaction of **1** with "$(CO)_4Fe$" to lead to **2c**, it was clear from the ^1H NMR data that this isomer was not formed (two different Cp groups **) from **1b**. The actual structure **2b**, is closely related to this *closo* form except that the more electron-poor iron center is coordinated by the better electron-donating μ-phosphido groups. The carbonyl groups associated with the molydenum atoms are semi-bridging, with deviations from linearity of about 17°. On simple electron counting grounds, **2b** is unsaturated with 46 valence electrons, and the unsaturation is apparent in the MoMo bond length (2.694 Å), which is considered to be in the range of a double bond [6]. The FeMo bond lengths are at the high end of the single bond range, although the only complexes structurally characterized which contain this type of bond have μ-S, μ-SR, as well as one case of μ^3-PR, supporting ligands [7].

A complex **3** containing the mono-unsaturated Mo_2Fe triangle has been proposed, but because of its extreme air and thermal lability, it could be characterized only spectroscopically [8]. A 48-electron oxo-capped analog of **3**, with pentamethylcyclopentadienyls in place of the Cp groups, has been characterized by X-ray

---

* *Crystal and data collection data for* **2a**, **2b**: The structures of **2a** and **2b** were determined using intensity data collected with Mo-K radiations at $-110\,^{\circ}C$ by the ω scan on a Syntex P21 diffractometer ($4^{\circ} \leqslant 2\theta \leqslant 55^{\circ}$). Both data sets were corrected for absorption. Refinements were carried out by using the program SHELX 76. Crystal data for **2a**: asymmetric unit, $C_{33}H_{24}O_5P_2Mo_2Fe\cdot 0.5C_4H_8O$, F.W. 810.2, $F(000) = 804$, d_{cal} 1.661 g cm^{-3} ($-110\,^{\circ}C$), triclinic, $P1$, with a 10.946(6) Å, b 17.667(6) Å, c 9.532(2) Å, α 105.45(2)°, β 112.94(3)°, γ 91.17(3)°, V 1620 Å^3, $Z = 2$, 7456 unique reflections and μ 13.23 cm^{-1}. The structure was solved by heavy atom methods and refined by full-matrix least-squares procedures to a final value of $R = 0.0297$ and $R_w = 0.0327$ using 6377 reflections with $|F_0| > 4.0\sigma(F_0)$. Both the phenyl rings and the two cp rings were refined as rigid groups. The phenyl ring on P(1) and the cp ring on Mo(1) are disordered. Their occupancies were refined to 0.63 and 0.37 (phenyl) and 0.68 and 0.32 (cp). Crystal data for **2b**: $C_{29}H_{32}O_5P_2Mo_2Fe\cdot 0.5C_7H_8$, F.W. 810.22, $F(000) = 804$, d_{cal} 1.689 g cm^{-3} ($-110\,^{\circ}C$), d_{obs} 1.674 g cm^{-3} ($25\,^{\circ}C$), monoclinic $C2/c$ with a 17.508(9) Å, b 12.064(6) Å, c 33.144(17) Å, β 114.43(5)°, V 6374.0 Å^3, $Z = 8$, 7327 unique reflections, and μ 13.43 cm^{-1}. The structure was solved by heavy atom methods and refined by full matrix least squares procedures to a final $R = 0.0558$ and $R_w = 0.0411$ for 4266 reflections with $|F_0| > 4.0\sigma(F_0)$. Methyl groups were refined as rigid groups. The atomic coordinates for this work are available on request as NAPS document no. 04583, 97 pages. Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163-3513. Remit in advance, in U.S. Funds only, $30.85 for photocopies or $4.00 for microfiche. Outside the U.S.A. and Canada, add postage of $4.50 for the first 20 pages and $1.00 for each of 10 pages of material thereafter, or $1.50 for microfiche postage.

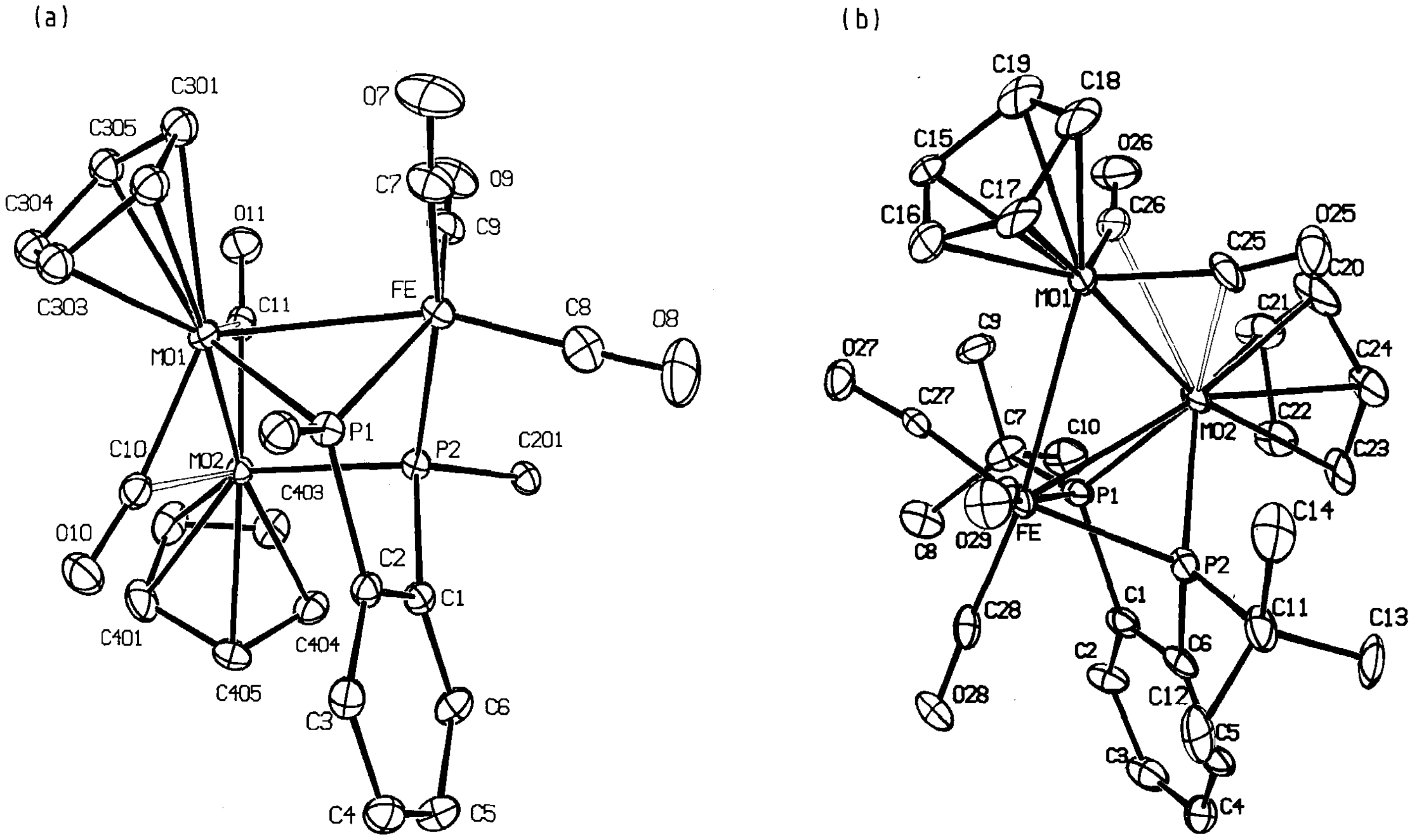


Fig. 1. (a) ORTEP view of **2a**. The phenyl groups are shown only as their *ipso* carbons, C(101) (not labeled) at P(1) and C(201) at P(2). The Cp carbons, C(302) and C(402), are not labeled. Selected bond lengths (Å): Mo(1)–Mo(2) 2.5369(11), Mo(1)–Fe 2.8553(10), Mo(1)–P(1) 2.4334(12), Mo(1)–C(10) 1.962(4), Mo(1)–C(11) 2.591(3), Mo(2)–P(2) 2.4270(10), Mo(2)–C(11) 1.930(4), Mo(2)–C(10) 2.323(3), Mo(2)...Fe 3.889(1), Fe–P(2) 2.2826(11), Fe–P(1) 2.1840(14); selected angles (°): Mo(1)–P(1)–Fe 76.18(4), Mo(2)–P(2)–Fe 111.28(4), Mo(1)–C(10)–O(10) 162.1(2), Mo(2)–C(11)–O(11) 167.7(2), C(10)–Mo(1)–Mo(2)-C(11) 148.3(1). (b) ORTEP view of **2b**. Selected bond lengths (Å): Mo(1)–Mo(2) 2.6941(15), Mo(1)–Fe 2.920(2), Mo(1)–C(25) 1.921(9), Mo(1)–C(26) 1.931(9), Mo(2)–Fe 2.868(2), Mo(2)–P(1) 2.349(2), Mo(2)–P(2) 2.350(2), Mo(2)–C(25) 2.558(8), Mo(2)–C(26) 2.514(8), Fe–P(1) 2.279(3), Fe–P(2) 2.274(3); selected angles (°): Mo(1)–Fe–Mo(2) 55.47(4), Fe–Mo(1)–Mo(2) 61.29(5), Fe–Mo(2)–Mo(1) 63.25(5), Mo(2)–P(1)–Fe 76.57(7), Mo(2)–P(2)–Fe 76.66(7), Mo(1)–C(25)–O(25) 163.7(6), Mo(1)–C(26)–O(26) 162.2(7), P(1)–Mo(2)–Mo(1)–C(26) −90.5(3), P(2)–Mo(2)–Mo(1)–C(25) 93.4(3).

crystallography [9,10*]. This material arose from apparent dioxygen scavenging from the reaction solution, and the unsaturated Cp * analog **3** could not be isolated. The fact that we have been able to isolate and fully characterize **2b** is indicative of stabilizing effect of the linked bis(μ-phosphido) ligand on such labile metal–metal bonds. It also illustrates how sensitive cluster structures are to apparently subtle differences in the ligand.

Acknowledgements. We thank the National Science Foundation and the Robert A. Welch Foundation for financial support.

References

1 E.P. Kyba, R.E. Davis, C.N. Clubb, S.-T. Liu, H.O.A. Palacios, J.S. McKennis, Organometallics, 5 (1986) 869.
2 E.L. Muetterties, Bull. Soc. Belg., 84 (1975) 959; E.L. Muetterties, Science, (1977) 839.
3 B.F.G. Johnson (Ed.), Transition Metal Clusters, Wiley, New York, 1980.
4 R. Hoffmann, Angew. Chem., Int. Ed. Eng., 21 (1982) 711.
5 E.P. Kyba, J.D. Mather, K.L. Hassett, J.S. McKennis, R.E. Davis, J. Am. Chem. Soc., 106 (1984) 5371.
6 A.L. Rheingold, M.J. Foley, P.J. Sullivan, J. Am. Chem. Soc., 104 (1982) 4727, and references therein; M.D. Curtis, L. Messerle, J.J. D'Errico, H.E. Solis, I.D. Barcelo, W.M. Butler, ibid., 109 (1987) 3603.
7 P.D. Williams, M.D. Curtis, D.N. Duffy, W.M. Butler, Organometallics, 2 (1983) 165, and ref. therein; B. Cowans, J. Noordik, M. Rakowski DuBois, ibid., 2 (1983) 932; F. Richter, H. Vahrenkamp, Chem. Ber., 115 (1982) 3243; S. Lu, N. Okura, T. Yoshida, S. Otsuka, K. Hirotsu, T. Higuchi, J. Am. Chem. Soc., 105 (1983) 7470; M. Muller, H. Vahrenkamp, Chem. Ber., 116 (1983) 2748.
8 M.D. Curtis, R.J. Klingler, J. Organomet. Chem., 161 (1978) 23.
9 C.P. Gibson, J.-S. Huang, L.F. Dahl, Organometallics, 5, (1986) 1676.
10 Very recently, the structure of a 46-electron *closo*-Mo_2Fe cluster with the unsaturation in the Mo_2 bond and a FeMo-coordinated bis(*p*-tolyl)acetylene has been determined: M.E. Garcia, J.C. Jeffery, P. Sherwood, F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1987) 1209.

---

* A reference number with an asterisk indicates a note in the list of references.