Organometallics 1983, *2*, 1481–1483

Heterobimetallic Oxidative Addition of CH_3I to the Polar Rh–Mo Bond of $(C_5Me_5)\overline{Rh(\mu\text{-}PMe_2)_2Mo}(CO)_4$

Richard G. Finke* and Glen Gaughan

Department of Chemistry, University of Oregon
Eugene, Oregon 97403

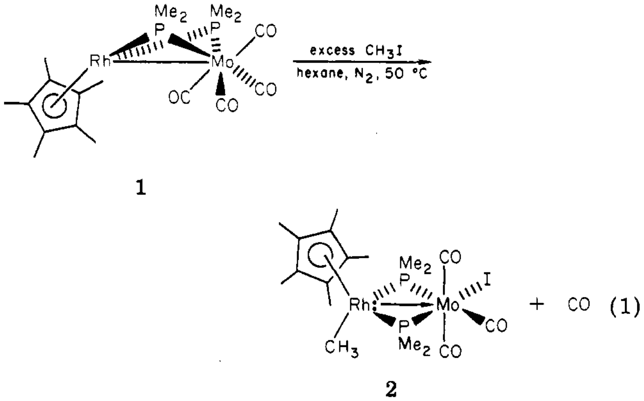
Cortlandt Pierpont* and Jan H. Noordik

Department of Chemistry, University of Colorado
Boulder, Colorado 80309

Received May 25, 1983

Summary: Regiospecific oxidative addition of CH_3I to the polar Rh–Mo bond of $(C_5Me_5)\overline{Rh(\mu\text{-}PMe_2)_2Mo}(CO)_4$ produces $(C_5Me_5)(CH_3)\overline{Rh(\mu\text{-}PMe_2)_2Mo}(CO)_3I$ and CO. The solid-state structure of the product was obtained and provides an interesting comparison to that of the starting Rh–Mo compound; the regiospecific lability and apparent one-electron mechanism of formation of the CH_3Rh–MoI product are also discussed.

Alkyl halide oxidative addition[1a,b] across a polar, heterobimetallic metal–metal bond has not been previously reported[2] in spite of the interest in heterobimetallic complexes,[2a,3] their structures, reactivity patterns, and, ultimately, their stoichiometric or catalytic reactions.[4,5] This report describes the oxidative addition of CH_3I to $(C_5Me_5)\overline{Rh(\mu\text{-}PMe_2)_2Mo}(CO)_4$ (**1**)[6] to give $(C_5Me_5)(CH_3)\overline{Rh(\mu\text{-}PMe_2)_2Mo}(CO)_3I$ (**2**) and 1 equiv of CO (eq 1). A determination of the crystal structure of **2** and its comparison to that of **1** reveal the regioselectivity of the oxidative addition as well as some interesting structural consequences of polar R–X addition to a polar Rh–Mo bond.



The reaction, eq 1, affords the moderately air and thermally stable ($t_{1/2} \approx 1$ day, 25 °C, N_2, THF) green product **2** in variable[7a] yield (≤80%). ^1H and ^{31}P NMR, IR, and FAB mass spectra were used to characterize[7b] **2** prior to a crystallographic molecular structure determination[8] on crystals grown from CH_2Cl_2/hexane.

Figure 1 provides a view of $(C_5Me_5)(CH_3)\overline{Rh(\mu\text{-}PMe_2)_2Mo}(CO)_3I$ (**2**), and a comparison of the central RhP_2Mo rings of **1**[6a] and **2** is provided in the diagram

---

[1] (a) Collman, J. P.; Hegedus, L. S. In "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; Chapter 4. (b) Finke, R. G.; Schiraldi, D. A.; Hirose, Y. *J. Am. Chem. Soc.* **1981**, *103*, 1875. Reference 2 therein provides a recent compilation of oxidative-addition references.

[2] Numerous reports, but few detailed mechanistic studies, of oxidative additions to *homobimetallic* complexes have appeared: (a) Chisholm, M. H., Ed. "Reactivity of Metal-Metal Bonds"; American Chemical Society: Washington, DC, 1981; *ACS Symp. Ser.* No. *155*, Chapter 8, see pp 25, 243–253 and references therein. See also: Chisholm, M. H.; Rothwell, I. P. *Prog. Inorg. Chem.* **1982**, *29*, 1 and references therein. (b) Lewis, N. S.; Mann, K. R.; Gordon J. G., II; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 7461. Che, C.-M.; Schaefer, W. P.; Gray, H. B.; Dickson, M. K.; Stein, P. B.; Roundhill, D. M. *Ibid.* **1982**, *104*, 4253. (c) Collman, J. P.; Rothrock, R. R.; Finke, R. G.; Moore, E. J.; Rose-Munch, F. *Inorg. Chem.* **1982**, *21*, 146. (d) Sumner, C. E.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 1752. Other examples of CH_2X_2 binuclear oxidative addition have appeared: Balch, A. L.; Hunt, C. T.; Lee, C.-L.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764. Jandik, P.; Schubert, U.; Schmidbaur, H. *Angew. Chem., Int. Eng. Ed.* **1982**, *21*, 73. Motyl, K. M.; Norton, J. R.; Schauer, C. K.; Anderson, O. P. *J. Am. Chem. Soc.* **1982**, *104*, 7325. (e) Schore, N. E.; Ilenda, C.; Bergman, R. G. *Ibid.* **1976**, *98*, 7436. (f) Theopold, K. H.; Bergman, R. G. *Ibid.* **1980**, *102*, 5694; *Organometallics* **1982**, *1*, 219. (g) Hersch, W. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 6992. (h) Haines, R. J.; de Beer, J. A.; Greatrex, R. *J. Chem. Soc. Dalton Trans.* **1976**, 1749. (i) Schmidbaur, H.; Franke, R. *Inorg. Chim. Acta* **1975**, *13*, 85. Schmidbaur, H.; Mandl, J. R.; Frank, A.; Hüttner, G. *Chem. Ber.* **1976**, *109*, 466. (j) Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 2267. Balch, A. L.; La Badie, J. W.; Delker, G. *Ibid.* **1979**, *18*, 1225. Balch, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 8049. (k) Poilblanc, R. *Nouv. J. Chem.* **1978**, *2*, 145. Poilblanc, R. *Inorg. Chim. Acta* **1982**, *62*, 75. (l) Thorez, A.; Maisonnat, A.; Poilblanc, R. *J. Chem. Soc. Chem. Commun.* **1977**, 518. (m) Mayanza, A.; Bonnet, J. J.; Galy, J.; Kalck, P.; Poilblanc, R., *J. Chem. Res., Synap.* **1980**, 146; *J. Chem. Res. Miniprint* **1980**, 2101. Bonnet, J. J.; Thorez, A.; Maisonnat, A.; Galy, J.; Poilblanc, R. *J. Am. Chem. Soc.* **1979**, *101*, 5940. Bonnet, J. J.; Kalck, P.; Poilblanc, R. *Angew. Chem., Int. Eng. Ed.* **1980**, *19*, 551. (n) Kalck, P.; Bonnet, J. J. *Organometallics* **1982**, *1*, 1211. CH_3I oxidative addition to $Ir_2(\mu\text{-}t\text{-}BuS)_2(CO)_2L_2$ yields appreciable amounts of the diiodide adduct, and the possibility of a one-electron mechanism was noted. (o) Coleman, A. W.; Eadie, D. T.; Stobart, S. R.; Zaworotko, M. J.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 922. (p) Sattelberger, A. P.; Wilson, R. B.; Huffman, J. C. *Ibid.* **1980**, *102*, 7111. (q) Cotton, F. A.; Mott, G. N. *Ibid.* **1982**, *104*, 5978. (r) Fackler, J. P.; Basil, J. D. *Organometallics* **1982**, *1*, 871. (s) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2733. (t) Petrignani, J. F.; Alper, H. *Organometallics* **1982**, *1*, 1095. (u) Brunner, H.; Meier, W.; Wachter, J.; Guggolz, E.; Zahn, T.; Ziegler, M. L. *Ibid.* **1982**, *1*, 1107. (v) Herrmann, W. A.; Plank, J.; Riedel, D.; Ziegler, M. L.; Weidenhammer, K.; Guggolz, E.; Balbach, B. *J. Am. Chem. Soc.* **1981**, *103*, 63. (w) Reference 14c.

[3] For a recent review of heterobimetallic complexes see: Robert, D. A.; Geoffroy, G. L. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergammon Press: Oxford, 1982.

[4] Of interest to the present study are the following: (a) Pugach, J.; Kus, H. H. US Patent 4251458 (Halcon Research and Development Corp), Feb 1981. This patent describes catalysis of $CH_3CO_2CH_3 \rightarrow CH_3C(O)OC(O)CH_3$ by an unspecified catalyst prepared in situ from, for example, $RhCl_3$, $Cr(CO)_6$, CH_3I, and Ph_3As. (b) Ellgen, P. C.; Bhasin, M. M. US Patent 4096164 (Union Carbide Corp), June 1978. This patent reports supported Rh/Mo as a preferred catalyst for $CO + H_2 \rightarrow C_2$ oxygenated hydrocarbons. (c) A Rh=Mo complex has been recently described: Carlton, L.; Lindsell, W. E.; McCullough, K. J.; Preston, P. N. *J. Chem. Soc. Chem. Commun.* **1982**, 1001.

[5] (a) Foley, H. C.; Finch, W. C.; Pierpont, C. G.; Geoffroy, G. L. *Organometallics* **1982**, *1*, 1379. See the discussion and ref 3 therein. This work also describes HCl oxidative addition to a Ru–Co heterobimetallic. (b) Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 53. This work and other studies by Geoffroy and co-workers[5c] and Carty and co-workers[5d] demonstrate that at least some phosphido-bridged complexes are less robust with more reactive PR_2 bridges than was generally believed several years ago. Additional quantitative studies of $M–XR_2–M'$ degradation for M, M′ = second- and third-row metals (X = As[5e] and P) and under controlled conditions of CO, H_2, RX, temperature, polar vs. nonpolar solvents, etc. would be useful. (c) Breen, M. J.; Geoffroy, G. L. *Organometallics* **1982**, *1*, 1437. (d) MacLaughin, S. A.; Carty, A. J.; Taylor, N. J. *Can. J. Chem.* **1982**, *60*, 87. (e) Casey, C. P.; Bullock, R. M. *J. Mol. Catal.* **1982**, *14*, 283.

[6] (a) Finke, R. G.; Gaughan, G.; Pierpont, C.; Cass, M. E. *J. Am. Chem. Soc.* **1981**, *103*, 1394. (b) Our initial report[6a] of the electrochemistry of **1** has been supplemented and, in part, corrected by additional studies demonstrating two one-electron oxidation and two one-electron reduction waves for **1** in THF at 25 °C, $E_{1/2} = -0.035$ V, $+0.455$ V and $E_{1/2} = -1.62$ V, $E_{pc} = -1.94$ V (50 mV/s) vs. SCE, respectively.

[7] (a) Poorer yields of **2** are observed if the CO pressure formed during the reaction, eq 1, is not released and if extended reaction times are used due to the thermal instability of **2** (although **2** is largely insoluble in hexane). (b) Complete details will be published in a subsequent full paper.

0276-7333/83/2302-1481$01.50/0

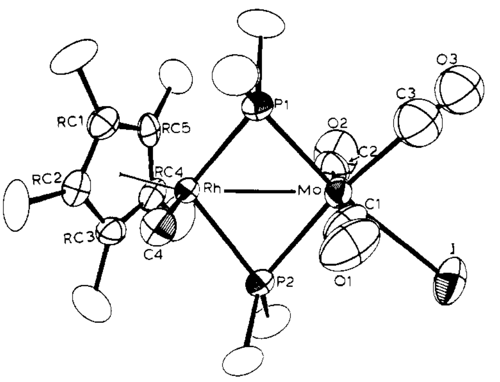
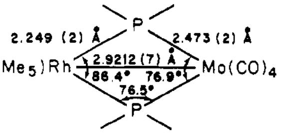
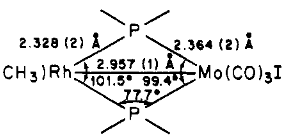


Figure 1. An ORTEP drawing of $(C_5Me_5)(CH_3)Rh(\mu\text{-}PMe_2)_2Mo(CO)_3I$. Selected bond lengths (Å) in addition to those shown in the diagram are as follows: Rh–C(4) = 2.112 (12), Mo–I = 2.855 (1), Mo–C(1) = 2.005 (14), Mo–C(2) = 2.076 (13), and Mo–C(3) = 2.034 (18).

below. Several features are of interest: (a) the CH_3I oxidative addition is regioselective if not regiospecific, with only $CH_3Rh\text{-}MoI$ (>80%) but no $IRh\text{-}MoCH_3$ (^1H NMR) identified to date; (b) the acute interior bond angles and the resultant nonplanar, bicyclobutane-like structure for 1 are replaced by an approximately planar RhP_2Mo core in 2; (c) the Rh–P bond lengths increase by roughly 0.1 Å in 2 compared to that for 1, the expected result of Rh oxidation and decreased Rh–P π bonding, yet the Mo–P lengths *decrease* by over 0.1 Å, a result opposite to the Mo–P bond increase observed upon formal oxidation of the *homobimetallic* $[Cp(CO)_2Mo(\mu\text{-}PMe_2)Mo(CO)_3Cp]^-$ by proton addition;[9] (d) the Rh–Mo separation in 2 is only about 0.036 Å greater than in 1, suggesting that eq 1 proceeds with retention of the Rh–Mo bond in 1; and (e) the I^- in 2 occupies, somewhat surprisingly, the coordination site yielding the *mer* rather than the *fac* isomer at molybenum.



1



2

^{31}P NMR and IR data compliment the crystallographic data on 2 by supporting the presence of a Rh–Mo bond and addressing the question of the charge distribution in 2, respectively. The ^{31}P resonances for 1 (δ ($CDCl_3$) 167.6 (d, $J_{Rh\text{-}P}$ = 133 Hz)) and 2 (δ ($CDCl_3$) 183.0 (d, $J_{Rh\text{-}P}$ = 80 Hz) and 163.5 (d, $J_{Rh\text{-}P}$ = 82 Hz))[10] both occur in the downfield region now associated with phosphido ligands bridging bonded metal atoms.[9,11] The charge distribution in 2 appears to be roughly that expected for CH_3I addition across the formally Rh(II)–Mo(I) bond in 1 to yield CH_3Rh^{III}: $\rightarrow$ $Mo^{II}I$, with a dative Rh: $\rightarrow$Mo bond. There is, however, some evidence of a contributing Rh(IV)–Mo(I) structure.[12] A Mo(I) formulation is suggested by the similar, average Mo–CO(trans) bond lengths in 1 and 2 (2.041 Å), the comparable ν_{CO} ($CDCl_3$) = 2005, 1940, and 1910 cm^{-1} and 2010, 1977, and 1895 cm^{-1} for 1 and 2, respectively, and, perhaps, by the short Mo–P distance in 2 and its implied greater Mo–P π bonding.

While several of the results presented herein can be qualitatively understood by using the available theoretical models for 34 valence electron, phosphido-bridged complexes,[13] a fuller understanding will require similar molecular orbital studies on 1 and 2. The regioselectivity observed in eq 1 is especially interesting in light of data[14] that points toward a one-electron, electron-transfer and/or radical chain[14c] mechanism, an atypical *CH_3I* oxidative-addition mechanism.[15] The regiospecific lability of 2, consistent with its long 2.855 (1) Å Mo–I bond, is also significant. Conductivity studies demonstrate that the I^- easily and reversibly dissociates in polar, coordinating solvents like acetone, CH_3CN, or Me_2SO while the ^1H NMR showed that the Rh-bound C_5Me_5 and CH_3 groups (but not the P-CH_3 $X_3AA'X'_3$ groups) remained unchanged. This regiospecific lability suggests that the oxidative-addition product 2 may serve as an important starting material for the synthesis of well-defined "$CH_3Rh\text{-}MoR$" (R = R, H, D, olefins, RNC, etc.) complexes and for needed fundamental studies of heterobimetallic insertion and reductive-elimination reactions.[16]

Acknowledgment. Financial support at Oregon was provided by NSF Grant CHE-8018199 and FAB mass spectra were obtained with the assistance of Professor Kenneth Suslick at the University of Illinois. R.G.F. is a Dreyfus Teacher-Scholar (1982–1987) and an Alfred P. Sloan Foundation Fellow (1982–1984).

---

(8) Crystals of 2 from CH_2Cl_2/hexane form in the acentric monoclinic space group C_C. Cell constants of a = 8.593 (2) Å, b = 17.593 (5) Å, c = 16.715 (7) Å, β = 103.98 (2)°, and V = 2452 (1) $Å^3$ were determined from the centered settings of 25 high-angle reflections (Mo K α radiation). The intensities of 3937 reflections were measured by using an automated diffractometer, 2185 of which had $F_o^2 > 3\sigma(F_o^2)$, and were included in the refinement. The structure was solved by using MULTAN-2. Least-squares refinement of the complete structure converged with R = 0.042 and R_w = 0.045. Slight disorder between the I atom and the CO(3) carbonyl ligand contributed to an anomalously short C–O(3) length of 1.00 Å and a negative thermal parameter for oxygen O(3).

(9) Petersen, J. L.; Stewart, R. P. *Inorg. Chem.* **1980**, *19*, 186–191.

(10) (a) No attempt was made to resolve $J_{P\text{-}P'}$, which is often $J_{P\text{-}P'}$ = ca. 20 Hz[10b] for planar $M(\mu\text{-}PR_2)_2M'$ systems. (b) Dessy, R. E.; Rheingold, A. L.; Howard, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 746.

(11) Carty, A. J., *Adv. Chem. Ser.* **1982**, *No.* **196**, 163.

(12) Maitlis has prepared a $(C_5Me_5)Rh^{IV}$ derivative: Fernandez, M.-J.; Maitlis, P. M. *J. Chem. Soc. Chem. Commun.* **1982**, 310.

(13) (a) The available studies show the greater significance of the M–P rather than the M–M interactions[13b] and the importance, via Walsh diagrams, of competing M–M bonding and M–P antibonding a_1 symmetry and M–M antibonding and M–P bonding b_2 symmetry orbitals in the case of $(OC)_3Co(\mu\text{-}PH_2)_2Co(CO)_3$, for example. (b) Burdett, J. K. *J. Chem. Soc. Dalton Trans.* **1977**, 423. (c) Pinhas, A. R.; Hoffmann, R. *Inorg. Chem.* **1979**, *18*, 654.

(14) (a) The variable reaction times required (up to several hours), the variable yields of 2, the failure of the reaction in THF coupled with work by Lappert et al.,[14b] and the two, one-electron, reversible oxidation waves for 1 in THF[6b] point toward a one-electron, oxidative-addition mechanism. A detailed mechanistic study is underway. (b) Gynane, M. J. S.; Lappert, M. F.; Miles, S. J.; Power, P. P. *J. Chem. Soc. Chem. Commun.* **1978**, 192. Hall, T. L.; Lappert, M. F.; Lednor, P. W. *J. Chem. Soc. Dalton Trans.* **1980**, 1448. (c) Evidence for a photoinduced radical chain mechanism for a dimeric Rh(I) complex recently appeared: Fukuzumi, S.; Nobuaki, N.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 709.

(15) (a) Eberson, L. *Acta Chem. Scand., Ser. B* **1982**, *36B*, 533. Consistent with many earlier studies,[16,15b] this paper concludes that methyl halides favor "nucleophilic" rather than electron-transfer pathways in their monometallic oxidative additions. A one electron mechanism for CH_3I in eq 1 is, therefore, of interest.[15c] (b) For example see: Labinger, J. A.; Osborn, J. A. *Inorg. Chem.* **1980**, *19*, 3230. Labinger, J. A.; Osborn, J. A.; Coville, N. J. *Ibid.* **1980**, *19*, 3236. (c) Chanon, M. *Bull. Soc. Chim. Fr.* **1982**, II, 197.

(16) (a) Halpern, J. *Inorg. Chim. Acta* **1982**, *62*, 311. (b) Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360.