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## References and Notes

- (1) (a) D. Coucouvanis, D. G. Holah, C. Murphy, and S. Kanodia, paper presented at the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Sept 1976; (b) I. G. Dance and J. C. Calabrese, *Inorg. Chim. Acta*, **19**, L41 (1976); (c) E. H. Griffith, G. W. Hunt, and E. L. Amma, *J. Chem. Soc., Chem. Commun.*, 432 (1976).
- (2) (a) R. Hesse, *Ark. Kemi*, **20**, 481 (1963); (b) S. L. Lawton, W. J. Rohrbach, and G. T. Kokotailo, *Inorg. Chem.*, **11**, 612 (1972).
- (3) I. G. Dance, *J. Chem. Soc., Chem. Commun.*, 103 (1976).
- (4) I. G. Dance, *J. Chem. Soc., Chem. Commun.*, 68 (1976).
- (5) (a) L. E. McCandish, E. C. Blssett, D. Coucouvanis, J. P. Fackler, and K. Knox, *J. Am. Chem. Soc.*, **90**, 7357 (1968); (b) F. J. Hollander and D. Coucouvanis, *ibid.*, **96**, 5646-5648 (1974).
- (6) H. Schugar, C. Ou, G. A. Thich, J. A. Potenza, R. A. Lalancette, and W. Furey, Jr., *J. Am. Chem. Soc.*, **98**, 3047 (1976).
- (7) P. J. M. W. L. Birker and H. C. Freeman, *J. Chem. Soc., Chem. Commun.*, 312 (1976).
- (8) F. J. Hollander and D. Coucouvanis, *J. Am. Chem. Soc.*, in press.
- (9) (a) D. Coucouvanis and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **89**, 1346 (1967). (b) The sulfur addition reaction to 1,1-dithiolate ligands in cluster complexes has been observed in our laboratory in the reactions of  $Cu_6(t-Bu-DED)_6$  with elemental sulfur. The crystal structure of one of the reaction products,  $BzPh_3PCu_5(t-Bu-DEDS)_4^-$ , unequivocally shows the presence of perthiolate ligands.
- (10) M. L. Cafferty, Ph.D. thesis, University of Iowa, 1973; M. L. Cafferty, R. Pedelty, and D. Coucouvanis, unpublished work.
- (11) P. Hemmerich and S. Sigwart, *Experientia*, **19**, 488 (1963).
- (12) The following abbreviations are used:  $Ph_4P$  = tetraphenylphosphonium,  $BzPh_3P$  = benzyltriphenylphosphonium,  $Bu_4N$  = tetrabutylammonium,  $Dtc$  = diethyldithiocarbamate,  $Dtp$  = diethyl dithiophosphate.
- (13) D. Coucouvanis, M. O'Connor, R. Pedelty, and W. Richardson, unpublished work.
- (14) Clear evidence for protonation of the methine carbon of the ligand is provided by the C-C-C angles around the three  $sp^2$ -hybridized methine carbons. For the three protonated ligands these angles are (a) 112.8 (9), 108.8 (9), 112.0 (9)°; (b) 114.2 (9), 108.1 (9), 110.0 (9)°; and (c) 113.2 (9), 111.2 (9), 111.0 (9)°. For the 1,1-dithiolate ligand the C-C-C angles found at the corresponding,  $sp^2$ -hybridized carbon atom are 125 (1), 120 (1), and 115 (1)°.

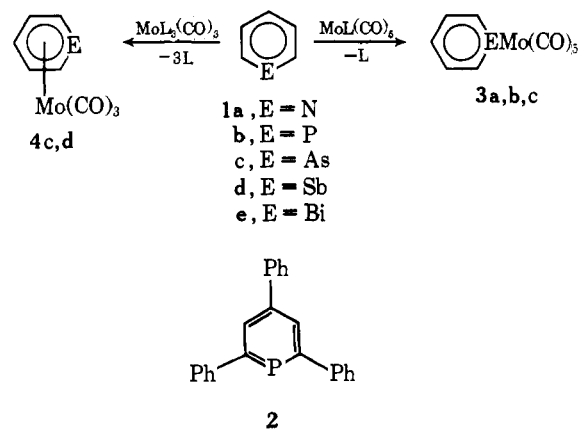
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## Molybdenum-Carbonyl Complexes of the Group 5 Heterobenzenes

Sir:

A variety of heteroaromatic compounds are known to act as both two-electron  $\sigma$  ligands and six-electron  $\pi$  ligands toward transition metals.<sup>1-4</sup> For example, pyridine (**1a**) readily forms  $\sigma$ -metal complexes while apparently only the 2,6-disubstituted pyridines easily give  $\pi$  complexes.<sup>2</sup> The highly

substituted pyridine analogue 2,4,6-triphenylphosphabenzene (**2**) also gives both  $\sigma$ -<sup>3</sup> and  $\pi$ -<sup>4</sup>metal-carbonyl complexes. The recent availability of the complete series of pyridine homologues **1b**,<sup>5</sup> **1c**,<sup>5</sup> **1d**,<sup>6</sup> and **1e**<sup>7</sup> has prompted us to undertake a comparative study of their  $\sigma$ - and  $\pi$ -coordination chemistry.



The  $\sigma$  complex, phosphabenzene-molybdenum pentacarbonyl (**3b**), may be readily prepared by ligand displacement from  $THF \cdot Mo(CO)_5$ . The complex is obtained as air-sensitive yellow crystals:<sup>8</sup> mp 76-77 °C; IR ( $CHCl_3$ ) 2078 (m), 1962 (s)  $cm^{-1}$  (CO); mass spectral parent peak at  $m/e$  334 for  $C_5H_5P^{98}Mo(CO)_5$ . Both the  $^1H$  and  $^{13}C$ -nmr chemical shift lues of  $\sigma$  complex **3b** are very similar to those of free phosphabenzene (Tables I and II). However, the marked divergence of the  $J_{PH}$  and  $J_{PC}$  values of **1b** and **3b** is an expected consequence of the difference in coordination at phosphorus.<sup>3,9</sup> Unlike the analogous complex of **2**,<sup>3,4</sup> **3b** was thermally stable to 200 °C and did not lose CO to form the expected  $\pi$  complex **4b**.

A similar reaction of arsabenzene (**1c**) with pyridine- $Mo(CO)_5$  and boron trifluoride etherate gave the  $\sigma$  complex arsabenzene-molybdenum pentacarbonyl (**3c**) as yellow air-sensitive crystals: mp 64-65 °C; IR ( $CHCl_3$ ) 2079 (w), 1986 (s)  $cm^{-1}$  (CO); mass spectral parent ion at  $m/e$  378 for  $C_5H_5As^{98}Mo(CO)_5$ . Like the phosphabenzene complex, the proton and carbon NMR spectra are almost identical with those of the free ligand. Pyrolysis of **3c** at 120 °C destroyed the complex, eventually leading to small quantities of arsabenzene-molybdenum tricarbonyl (**4c**). This  $\pi$  complex is more conveniently prepared by heating  $Mo(CO)_6$  with arsabenzene in diglyme or by the boron trifluoride etherate catalyzed ligand displacement from tris(pyridine)molybdenum tricarbonyl.

**Table I.** The Proton Chemical Shift Values<sup>a</sup> of the Heterobenzenemolybdenum Carbonyl Complexes<sup>b</sup> (with the Values for the Free Heterobenzenes in Parentheses<sup>c</sup>)

Position	<b>3b</b>	<b>3c</b>	<b>4c</b>	<b>4d</b>
$H_\alpha$ ( $H_2, H_6$ )	8.5, $^2J_{PH} = 26$ (8.6, $^2J_{PH} = 38$ )	9.6 (9.7)	5.9 (9.7)	6.1 (10.9)
$H_\beta$ ( $H_3, H_5$ )	7.7, $^3J_{PH} = 20$ (7.7, $^3J_{PH} = 8$ )	7.8 (7.8)	5.4 (7.8)	5.7 (8.2)
$H_\gamma$ ( $H_4$ )	7.4, $^4J_{PH} = 6$ (7.4, $^4J_{PH} = 3.5$ )	7.5 (7.5)	5.9 (7.5)	6.1 (7.8)

<sup>a</sup> The chemical shift values are quoted to the nearest 0.1 ppm and are measured downfield from internal TMS in  $CDCl_3$ . Phosphorus-proton coupling constants are in hertz. <sup>b</sup> The apparent chemical shift values have been taken as the centers of multiplets. <sup>c</sup> Reference 12.

**Table II.** The Carbon-13 Chemical Shift Values<sup>a</sup> of the Heterobenzenemolybdenum Carbonyl Complexes (with the Values for the Free Heterobenzenes in Parentheses<sup>b</sup>)

Position	<b>3b</b>	<b>3c</b>	<b>4c</b>	<b>4d</b>
$C_\alpha$ ( $C_2, C_6$ )	151.0, $^1J_{PC} = 12.7$ (154.1, $^1J_{PC} = 53$ )	164.5 (167.7)	110.8 (167.7)	114.6 (178.3)
$C_\beta$ ( $C_3, C_5$ )	137.2, $^2J_{PC} = 16.8$ (133.6, $^2J_{PC} = 14$ )	136.1 (133.2)	94.2 (133.2)	95.5 (134.4)
$C_\gamma$ ( $C_4$ )	127.2, $^3J_{PC} = 32.0$ (128.8, $^3J_{PC} = 22$ )	126.4 (128.2)	87.5 (128.2)	88.0 (127.4)

<sup>a</sup> The chemical shift values are measured in parts per million downfield from internal TMS in  $CDCl_3$ .  $J_{PC}$  values are in hertz. <sup>b</sup> Reference 12.

These air-stable red crystals have mp 109–110 °C; IR (CHCl<sub>3</sub>) 1996 (s), 1926 (m) cm<sup>-1</sup> (CO); mass spectral parent molecular ion at *m/e* 322 for C<sub>5</sub>H<sub>5</sub>As<sup>98</sup>Mo(CO)<sub>3</sub>.

The upfield shift of the NMR proton and carbon signals of **4c** relative to **1c** are similar to those observed in arene-metal complexes,<sup>10</sup> thus clearly demonstrating π complexation.<sup>11</sup> The three different ring protons of the π complex vary only slightly in their chemical shift values. In contrast, the corresponding protons of free arsabenzene are quite distinct with the α-proton signals nearly 2 ppm downfield from the β- and γ-proton signals. This effect has been attributed to the influence of the large arsenic atom anisotropy directed perpendicular to the ring plane.<sup>12</sup> It is thus particularly interesting that this effect is completely eliminated by π complexation perpendicular to the ring but unaffected by σ complexation in the ring plane.

We have not succeeded in preparing σ complexes of stibabenzene (**1d**) by methods used to prepare **3b** and **3c**. However, the π complex **4d** may be easily obtained by boron trifluoride etherate catalyzed ligand displacement from tris(pyridine)-molybdenum tricarbonyl. These air-stable red-brown crystals have mp 106–108 °C; IR (CHCl<sub>3</sub>) 1990 (s), 1919 (m) cm<sup>-1</sup> (CO); mass spectral parent peak ion at *m/e* 370 for C<sub>5</sub>H<sub>5</sub><sup>123</sup>Sb<sup>98</sup>Mo(CO)<sub>3</sub>. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **4d** are nearly identical with those of **4c**. Stibabenzemolybdenum tricarbonyl is considerably more stable than free stibabenzene. This suggests that, much like cyclobutadieneiron tricarbonyl,<sup>13</sup> the high energy π electrons of the ligand are stabilized by donation to the metal. Since the π-ionization potential of bismabenzene (**1e**) is even lower,<sup>14</sup> we anticipate that it should be even a stronger π base. As yet our efforts to produce **4e** have been frustrated by the extreme lability of bismabenzene.<sup>7</sup>

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## References and Notes

- (a) For pyrrole see K. K. Joshi, P. L. Pauson, A. R. Qazi, and W. H. Stubbs, *J. Organomet. Chem.*, **1**, 471 (1964); P. L. Pauson and A. R. Qazi, *ibid.*, **7**, 321 (1967). (b) For phosphole see E. H. Bray and K. K. Joshi, *Bull. Soc. Chim. Belg.*, **80**, 651 (1971); F. Mathey, A. Mitschler, and R. Weiss, *J. Am. Chem. Soc.*, **99**, 3537 (1977).
- H.-G. Biedermann, K. Oefele, N. Schuhbauer, and J. Tajtelbaum, *Angew. Chem., Int. Ed. Engl.*, **14**, 639 (1975). L. H. Simons, P. E. Riley, R. E. Davis, and J. J. Lagowski, *J. Am. Chem. Soc.*, **98**, 1044 (1976). However, see E. O. Fischer and K. Oefele, *Chem. Ber.*, **93**, 1156 (1960); P. L. Timms, *Angew. Chem., Int. Ed. Engl.*, **14**, 273 (1975).
- J. Deberitz and H. Noeth, *J. Organomet. Chem.*, **49**, 453 (1973); H. Vahrenkamp and H. Noeth, *Chem. Ber.*, **106**, 2227 (1973).
- J. Deberitz and H. Noeth, *Chem. Ber.*, **103**, 2541 (1970); **106**, 2222 (1973). H. Vahrenkamp and H. Noeth, *Chem. Ber.*, **105**, 1148 (1972).
- A. J. Ashe, III, *J. Am. Chem. Soc.*, **93**, 3293 (1971).
- A. J. Ashe, III, *J. Am. Chem. Soc.*, **93**, 6690 (1971).
- A. J. Ashe, III, and M. D. Gordon, *J. Am. Chem. Soc.*, **94**, 7596 (1972); A. J. Ashe, III, *Tetrahedron Lett.*, 415 (1976).
- Satisfactory C, H combustion analyses have been obtained on all new compounds.
- (a) For *J<sub>PH</sub>* values see S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Am. Chem. Soc.*, **89**, 5573 (1967). (b) For *J<sub>PC</sub>* values see O. A. Gansow and B. Y. Kimura, *Chem. Commun.*, 1621 (1970).
- V. Graves and J. J. Lagowski, *Inorg. Chem.*, **15**, 577 (1976); D. J. Thoenes, C. L. Wilkins, and W. S. Trahanovsky, *J. Magn. Reson.*, **13**, 18 (1974).
- Preliminary results from single crystal x-ray diffraction studies by J. C. Clardy and K. Hirotsu also indicate that **4c** and **4d** are π complexes.
- A. J. Ashe, III, R. R. Sharp, and J. W. Tolman, *J. Am. Chem. Soc.*, **98**, 5451 (1976).
- See M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds", Academic Press, New York, N.Y., 1967.
- C. Batic, E. Heilbronner, V. Hornung, A. J. Ashe, III, D. T. Clark, U. T. Cogley, D. Klicast, and I. Scanlan, *J. Am. Chem. Soc.*, **95**, 928 (1973); J. Bastide, E. Heilbronner, J. P. Maier, and A. J. Ashe, III, *Tetrahedron Lett.*, 411 (1976).

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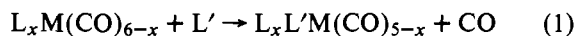
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## Site of Bond Breaking in Ligand-Exchange Reactions of 1,2-Bis-(diphenylphosphino)ethanetetracarbonylmolybdenum(0)<sup>1</sup>

Sir:

There is mounting evidence that the five-coordinate intermediates arising from metal-carbon bond breaking taking place during ligand-exchange reactions of octahedral metal carbonyls and derivatives, e.g.,



may be fluxional on the time scale of the substitution process. Thus, where the substrate possesses chemically nonequivalent carbonyls, it is not possible to infer the site of initial metal-carbon bond breaking from the stereochemistry of the reaction products, where  $L' \neq *CO$ .<sup>2</sup> However, a knowledge of that site is crucial to the development of bonding-reactivity relationships for such systems.<sup>3</sup>

An early, much-studied example is that which has been observed for the carbon monoxide exchange in manganese pentacarbonyl bromide.<sup>2,4</sup> The work of Brown and coworkers,<sup>5</sup> in which infrared spectroscopy was employed to determine the rates of substrate decay and of appearance and disappearance of the eleven possible <sup>13</sup>CO enrichment products, revealed that Mn-C bond breaking occurs exclusively at the equatorial positions (Br is axial), and that the resulting Mn(CO)<sub>4</sub>Br intermediate is fluxional. The Brown method has been applied to other systems as well, but in some instances the results have been less than unequivocal.<sup>6</sup>

Herein is presented an alternate procedure for the elucidation of the site of metal-carbonyl bond breaking which involves the study of molecules each containing only a single isotopic label, and the application of that procedure to (diphos)-Mo(CO)<sub>4</sub> (diphos = 1,2-bis(diphenylphosphino)ethane) in its reaction with cyclohexylamine. The key to the procedure is the stereospecific introduction of a single <sup>13</sup>CO label into the substrate under conditions much milder than those under which metal-carbonyl bond breaking takes place.

(diphos)Mo(CO)<sub>4</sub> reacts with Lewis bases (L) with replacement of a carbonyl to afford, depending upon the identity

**Scheme I.** Reaction Scheme for Determination of the Site of Bond Breaking in (diphos)Mo(CO)<sub>4</sub> and the Degree of Fluxionality of the Resulting [(diphos)Mo(CO)<sub>3</sub>] Intermediate for the Reaction of (diphos)Mo(CO)<sub>4</sub> with Cyclohexylamine. The Conversions **1a** → **1c** → **1e** Are Wholly Analogous.

