

the contrary, the absence of aromatic "layers" in a nematic medium allows higher translational diffusion along the director (D_n),¹² so one expects head-to-tail encounters to be promoted by the nematic solvent, as actually seems to result in the polymerization of phenylacetylene.²

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Phosphine Functionalized Macrocycles. A New Type of Bridging Ligand for the Synthesis of Heterometallic Complexes

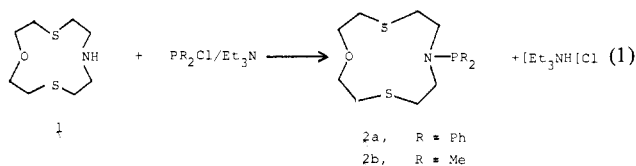
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Hybrid ligands in which a cyclopentadienyl and a phosphorus donor or a Schiff base and a phosphorus donor are combined have been recently described.¹ Interest in such ligands stems from their potential for the synthesis of new bimetallic complexes containing different metal centers in close proximity. We report the synthesis of a mono-P-donor ligand in which an amino-phosphine function and a macrocycle are combined. Several complexes of this unusual bridging ligand are described.

The 1-aza-4,10-dithia-7-oxacyclododecane ring, **1**,² may be derivatized by reaction with chlorodiphenylphosphine or chlorodimethylphosphine in the presence of 1 equiv of a tertiary amine, to give aminophosphine ligands **2a,b** (reaction 1). **2a,b** (CNPR_2),



obtained as colorless, air-sensitive oils on workup and characterized spectroscopically,³ have the potential to coordinate to two metal atoms, through the phosphine center and via the heteroatom donors of the ring.

2a ($R = \text{Ph}$) and **2b** ($R = \text{Me}$) react with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and $[(\text{CyO})_2\text{Ir}(\text{CO})\text{Cl}]_2$ ($\text{CyO} = \text{cyclooctene}$) (2 equiv of ligands/metal atom), to give the Vaska-type complexes *trans*- $[\text{Rh}(\text{CO})\text{Cl}(\text{CNPPH}_2)_2]$, **3** (ν_{CO} 1947 cm^{-1}), *trans*- $[\text{Ir}(\text{CO})\text{Cl}(\text{CNPPH}_2)_2]$, **4** (ν_{CO} 1947 cm^{-1}), and *trans*- $[\text{Rh}(\text{CO})\text{Cl}(\text{CNPM}_2)_2]$, **5** (ν_{CO} 1949 cm^{-1}) as fully characterized yellow-orange solids.⁴⁻⁶

(1) (a) Shore, N. E.; Hope, H. *J. Am. Chem. Soc.* **1980**, *102*, 4251. (b) Kraihanzel, C. S.; Sinn, E.; Gray M. G. *J. Am. Chem. Soc.* **1981**, *103*, 960.

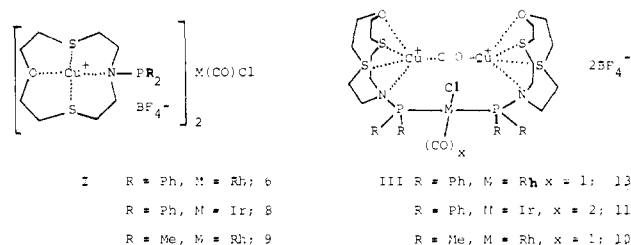
(2) Black, C. St. C.; McLean, I. A.; *Aust. J. Chem.* **1971**, *24*, 1401.

(3) **2a**: mass spectrum, parent ion 391 m/e^+ ; ^1H NMR (CDCl_3) δ 7.2-7.5 (m, 10 H), 2.4-3.5 (m, 16 H). **2b**: mass spectrum, parent ion 267 m/e^+ ; ^1H NMR (CDCl_3) 2.6-3.9 (m, 16 H), 1.10 (d, $J_{\text{P-H}} = 6$ Hz, 6 H). Both compounds show strong absorptions at ~ 730 cm^{-1} , attributable to the P-N stretching mode.

(4) Anal. Calcd for $\text{C}_{41}\text{H}_{52}\text{ClIrN}_2\text{O}_3\text{P}_2\text{RhS}_4$ (**3**): C, 50.87; H, 5.52; N, 2.95; Cl, 3.73; mol wt, 949. Found: C, 50.78; H, 5.21; N, 2.96; Cl, 3.50; mol wt, 927. Calcd for $\text{C}_{41}\text{H}_{52}\text{ClIrN}_2\text{O}_3\text{P}_2\text{S}_4$ (**4**): C, 47.47; H, 5.05; N, 2.70; Cl, 3.41; mol wt, 1039. Found: C, 48.66; H, 5.03; N, 2.77; Cl, 3.66; mol wt, 992. Calcd for $\text{C}_{21}\text{H}_{44}\text{ClN}_2\text{O}_3\text{P}_2\text{RhS}_4$ (**5**): C, 35.97; H, 6.33; N, 4.00; Cl, 5.06; mol wt, 691. Found: C, 36.73; H, 6.88; N, 4.03; Cl, 5.14; mol wt, 723. Molecular weights ($\pm 5\%$) were determined osmotically in CHCl_3 .

(5) The phosphorus methyl resonances of **5** appear as a 1:2:1 triplet at δ 1.60 ($J_{\text{P-H}} = 3$ Hz) in the ^1H NMR spectrum, implying a *trans* disposition of the **2b** ligands about the rhodium atom.

When an acetonitrile solution containing 2 equiv of $\text{Cu}(\text{MeCN})_4\text{BF}_4$ is added to a solution of **3** under argon, an orange precipitate, **6** (ν_{CO} 2005 cm^{-1}), is isolated on addition of methanol. Spectroscopic and analytical data are consistent with the complexation of one Cu(I) ion by each ring chelate in the complex.⁷ (i.e., structure I). Significantly, the addition of a single equivalent



of $\text{Cu}(\text{MeCN})_4\text{BF}_4$ to complex **3** gives an orange solid, **7**, whose infrared spectrum contains a single ν_{CO} absorption at 1980 cm^{-1} . These results indicate that a single Cu(I) is complexed by only one ring in each Rh compound before a second copper ion is coordinated to the remaining chelate ring and that complexation of Cu(I) decreases the donor properties of the Ph_2P group (increases ν_{CO}).

Similar treatment of $[(\text{CNPPH}_2)_2\text{Ir}(\text{CO})\text{Cl}]$, **4**, and $[(\text{CNPM}_2)_2\text{Rh}(\text{CO})\text{Cl}]$, **5**, with 2 equiv of $\text{Cu}(\text{MeCN})_4\text{BF}_4$ gives the corresponding bis(Cu(I)) adducts $[(\text{CuCNPPH}_2)_2\text{Ir}(\text{CO})\text{Cl}](\text{BF}_4)_2$, **8**, and $[(\text{CuCNPM}_2)_2\text{Rh}(\text{CO})\text{Cl}](\text{BF}_4)_2$, **9**.⁷⁻⁹

The dications **6**, **8**, and **9**, containing two ring-chelated copper(I) ions, exhibit some properties typical of Vaska-type compounds and others of a more unusual nature. Thus, for example, the iridium complex **8** oxidatively adds H_2 to give the expected dihydride $[(\text{CuCNPPH}_2)_2\text{Ir}(\text{CO})\text{ClH}_2](\text{BF}_4)_2$,¹⁰ which can also be obtained from **4** via oxidative addition of H_2 followed by reaction with 2 equiv of $\text{Cu}(\text{MeCN})_4\text{BF}_4$. Infrared studies (acetonitrile solution) indicate that both **8** and **9** react reversibly with CO. On exposure to CO **9** gives the acetonitrile solution species **10**, stable only under CO, with two ν_{CO} bands, at 2065 and 1989 cm^{-1} . **8** reacts reversibly with CO to give the acetonitrile solution species **11**, stable only under CO, with three ν_{CO} bands, at 2068, 2013, and 1963 cm^{-1} . It is well known that Vaska-type complexes form reversible CO adducts of formula $[\text{Ir}(\text{CO})_2\text{Cl}(\text{PR}_3)_2]$,¹¹ and complex **4**, containing no Cu(I), does indeed react reversibly with CO to form $[(\text{CNPPH}_2)_2\text{Ir}(\text{CO})_2\text{Cl}]$, **12**, as shown by the presence of two strong bands, at 1983 and 1930 cm^{-1} , in its solution IR spectrum. By analogy with **12**, the ν_{CO} bands at 1963 and 2013 cm^{-1} in the spectrum of **11** are likely associated with the Ir center. The ν_{CO} absorptions in the region of 2070 cm^{-1} found in **10** and **11** are possibly associated with a Cu(I)-CO-Cu(I) species. Osborn has reported that a bis(copper(I)) "earmuff" complex forms a CO adduct (of possible structure II) with ν_{CO} at 2070 cm^{-1} .¹² Analogy and molecular models suggest III as a possible structure for the CO adducts **10** and **11**. In contrast to the reversible reaction of **8** and **9** with CO, the dication **6** reacts with

(6) Reaction of **2b** with $[(\text{C}_8\text{H}_{14})_2\text{Ir}(\text{CO})\text{Cl}]_2$ gave only viscous yellow oils of indeterminate stoichiometry, on attempted workup.

(7) Anal. Calcd for $\text{C}_{41}\text{H}_{52}\text{B}_2\text{ClCu}_2\text{F}_8\text{IrN}_2\text{O}_3\text{P}_2\text{RhS}_4$ (**6**): C, 39.39; H, 4.19; N, 2.24; Cl, 2.84. Found: C, 40.06; H, 4.25; N, 2.80; Cl, 2.87. Calcd for $\text{C}_{41}\text{H}_{52}\text{B}_2\text{ClCu}_2\text{F}_8\text{IrN}_2\text{O}_3\text{P}_2\text{S}_4$ (**8**): C, 36.77; H, 3.91; N, 2.09; Cl, 2.64. Found: C, 37.14; H, 3.74; N, 2.19; Cl, 2.98. Calcd for $\text{C}_{21}\text{H}_{44}\text{B}_2\text{ClCu}_2\text{F}_8\text{N}_2\text{O}_3\text{P}_2\text{RhS}_4$ (**9**): C, 25.28; H, 4.44; N, 2.81; Cl, 3.55. Found: C, 25.93; H, 4.08; N, 2.84; Cl, 3.79.

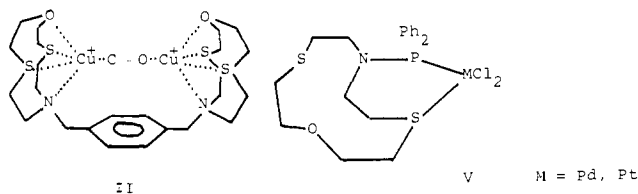
(8) The symbol CuCNPR_2 is used to indicate complexation of the Cu(I) ion by the aminophosphine ring.

(9) ^1H NMR for **9** (CD_3CN) δ 1.60 (1:2:1 br tr, 12 H, CH_3), 2.8-3.9 (m, 32 H, ring).

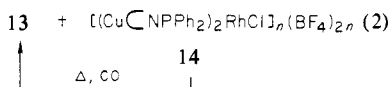
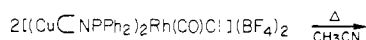
(10) Anal. Calcd for $\text{C}_{41}\text{H}_{54}\text{B}_2\text{ClCu}_2\text{F}_8\text{IrN}_2\text{O}_3\text{P}_2\text{S}_4$: C, 36.71; H, 4.06; N, 2.09; Cl, 2.64. Found: C, 36.18; H, 3.97; N, 2.11; Cl, 2.50. High-field ^1H NMR (CD_3CN) δ -9.41, -14.09 (each a 1:1 d of 1:2:1 tr, $J_{\text{P-H}} = 14$ Hz, $J_{\text{H-H}} = 3$ Hz). This dihydrido complex is very O_2 sensitive.

(11) Vaska, L. *Science* (Washington, D.C.) **1966**, *152*, 769. Payne, N. C.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 2714. Camia, M.; Zanzottera, C.; Delnoccantis, M. *Chim. Ind.* **1968**, *50*, 347.

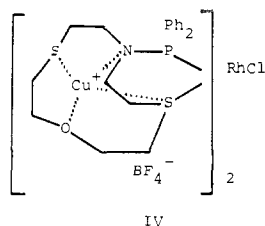
(12) Burkowski, J. E.; Burk, F. L.; Ludmann, M. F.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1977**, 498.



CO in acetonitrile solution only on reflux, and the dicarbonyl species $[(\text{CuCNPPH}_2)_2\text{Rh}(\text{CO})_2\text{Cl}](\text{BF}_4)_2$ (**13**; ν_{CO} bands at 2075 and 1987 cm^{-1}) may be isolated as a yellow solid.¹³ Surprisingly, if the dicationic complex **6** is refluxed in acetonitrile solution under an argon atmosphere for ca. 1 h, a disproportionation reaction occurs which can be observed by IR but is more easily investigated by ³¹P NMR spectroscopy. The spectrum of the dication **6** in $\text{CH}_3\text{CN}-d_3$ (δ P 31.74, $J_{\text{Rh-P}}$ 123 Hz) is transformed after a 1-h reflux (argon atmosphere) into a spectrum containing two 1:1 doublets of approximately equal intensities. One of these resonances (δ P 60.52, $J_{\text{Rh-P}}$ 96 Hz) corresponds very well with the ³¹P NMR spectrum of the dicarbonyl species **13**. The other (δ P 74.54, $J_{\text{Rh-P}}$ 118 Hz) is presumably due to a "carbonyl-free" Rh(I) complex, **14**, (i.e., reaction 2). When CO is bubbled



through a refluxing solution of **13** and **14**, the resonances due to **14** disappear and those of **13** grow in intensity; i.e., **14** reacts with CO to give **13**. The disproportionation (reaction 2) is, so far, unique to the dication **6**. Neither the dications **8** and **9** nor the "Cu⁺-free" complexes **3**, **4**, and **5** are affected by prolonged reflux in acetonitrile under argon. Although the exact nature of the species **14** is still under investigation, a plausible structure is IV. Support for P,S-bidentate complexation comes from the reaction **2a** with $\text{PdCl}_2(\text{PhCN})_2$, $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$, and $[(\text{COD})\text{RhCl}]_2/2\text{AgBF}_4$ (COD = cyclooctadiene) to give **15** (M = Pd, Pt, structure V) and $[(\text{COD})\text{RhPPH}_2\text{-N}(\text{D})\text{S}](\text{BF}_4)$, **16**.¹⁴



While the postulated structures II-IV are, at best, tenuous (and should be considered so until crystallographic data become available), the above results clearly indicate that phosphine functionalization of macrocyclic ligands is a viable route to new types of multimetallic systems. We are currently synthesizing metal carbonyl complexes of **2a,b** and their phosphine-derivatized aza-crown ether analogues with a view to promoting CO activation in a way analogous to previous studies involving chelating bisphosphinite complexes with crown ether properties.¹⁵

(13) Anal. Calcd for $\text{C}_{42}\text{H}_{52}\text{B}_2\text{ClCu}_2\text{F}_8\text{N}_2\text{O}_3\text{P}_2\text{RhS}_4$: C, 39.54; H, 4.01; N, 2.14; Cl, 2.71. Found: C, 39.09; H, 4.59; N, 2.37; Cl, 2.76.

(14) Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{Cl}_2\text{NOPPdS}_2$ (**15**, M = Pd): C, 42.23; H, 4.61. Found: C, 42.48; H, 4.72. IR data ($\nu_{\text{Pd-Cl}}$ 305 and 274 cm^{-1}) support a *cis*- PdCl_2 configuration. Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{Cl}_2\text{NOPPtS}_2 \cdot 0.5\text{CHCl}_3$ (**15**, M = Pt): C, 34.64; H, 3.27; N, 1.96; Cl, 17.63. Found: C, 34.33; H, 3.72; N, 1.95; Cl, 17.30. IR $\nu_{\text{Pt-Cl}}$ 320 and 283 cm^{-1} . Complexes **15** are too insoluble for NMR or molecular weight studies. However, **15** (M = Pt) reacts with $\text{Ti}(\text{acac})_3$ to give $\text{Ti}(\text{acac})_3\text{P}(\text{Ph})\text{P}(\text{Ph})\text{Cl}(\gamma\text{-acac})$, characterized by IR and ¹H NMR analysis. Anal. Calcd for $\text{C}_{28}\text{H}_{38}\text{BF}_4\text{NOPRHS}_2$ (**16**): C, 48.77; H, 5.50; N, 2.03. Found: C, 49.22; H, 5.73; N, 1.98.

(15) Powell, J.; Kuksis, A.; May, C. J.; Nyburg, S. C.; Smith, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 5941.

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Registry No. **1**, 24918-63-6; **2a**, 81157-79-1; **2b**, 81157-80-4; **3**, 81141-61-9; **4**, 81141-62-0; **5**, 81141-63-1; **6**, 81141-65-3; **7**, 81141-67-5; **8**, 81141-69-7; **9**, 81141-71-1; **10**, 81157-72-4; **11**, 81141-89-1; **12**, 81157-63-3; **13**, 81157-70-2; **14**, 81157-65-5; **15** (M = Pd), 81141-72-2; **15** (M = Pt), 81141-73-3; **16**, 81157-67-7; $\text{SCN-Ph}_2\text{P}(\text{Ph})\text{Cl}(\gamma\text{-acac})$, 81141-74-7; $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, 14404-25-2; $[(\text{CyO})_2\text{Ir}(\text{CO})\text{Cl}]_2$, 12119-19-6; $\text{Cu}(\text{MeCN})_4\text{BF}_4$, 15418-29-8; $[(\text{CuCNPPH}_2)_2\text{Ir}(\text{CO})\text{ClH}_2](\text{BF}_4)_2$, 81141-76-6; $\text{PdCl}_2(\text{PhCN})_2$, 14220-64-5; $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$, 12073-36-8; PPh_2Cl , 1079-66-9; PMe_2Cl , 811-62-1.

Characterization of the Vapor Species of Dilithiomethane by Flash Vaporization Mass Spectroscopy and the Ziegler Synthesis of Dilithiomethane

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The composition of the vapor species of the "electron-deficient" class of compounds, the lithiocarbons (C_nLi_m), is of widespread current interest. We report the first example of direct characterization and observation of the rather complex vapor species of polyolithium organic compounds.

The vapor species of dilithiomethane, $(\text{CH}_2\text{Li}_2)_n$, are of particular interest in view of the possibility proposed by the work of Schleyer, Pople, and co-workers¹ of the existence of fluxional *cis*, tetrahedral, and possibly *trans* gas-phase forms. Curiously, the first report of a polyolithium organic compound² (more than one lithium per carbon atom), the synthesis of $(\text{CH}_2\text{Li}_2)_n$ in 1955, went largely unnoticed until the early 1970s, when the field of polyolithium organic compounds was firmly established by synthetic work in the laboratories of Lagow,³ West,⁴ and others.⁵ This important Ziegler report went unrecognized, partly because it was 20 years ahead of its time and because it had gained a reputation for poor reproducibility in spite of a few reports of its derivative chemistry.⁶

Currently dilithiomethane, which may also be prepared by the reaction of lithium vapor with methylene chloride,⁷ is best prepared

(1) J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger, and J. A. Pople, *J. Am. Chem. Soc.*, **98**, 5419 (1976).

(2) K. Ziegler, K. Nagel, and M. Patheiger, *Z. Anorg. Allgem. Chem.*, **282**, 345 (1955).

(3) (a) C. Chung and R. J. Lagow, *J. Chem. Soc., Chem. Commun.*, 1970 (1972). (b) L. A. Shimp and R. J. Lagow, *J. Am. Chem. Soc.*, **95**, 1343 (1973). (c) L. G. Sneddon and R. J. Lagow, *J. Chem. Soc., Chem. Commun.*, 302 (1975). (d) J. A. Morrison, C. Chung, and R. J. Lagow, *J. Am. Chem. Soc.*, **97**, 5015 (1975). (e) J. A. Morrison and R. J. Lagow, *Inorg. Chem.*, **16**, 2972 (1977). (f) L. A. Shimp, C. Chung, and R. J. Lagow, *Inorg. Chim. Acta*, **29**, 77-81 (1978). (g) K. M. Abraham and R. J. Lagow, *Tetrahedron Lett.*, **3**, 211 (1979). (h) L. A. Shimp and R. J. Lagow, *J. Am. Chem. Soc.*, **101**, 2214 (1979). (i) L. A. Shimp and R. J. Lagow, *J. Org. Chem.*, **44**, 2231 (1979).

(4) (a) R. West and P. C. Jones, *J. Am. Chem. Soc.*, **91**, 6155 (1969). (b) G. A. Gornowicz and R. West, *ibid.*, **93**, 1720 (1971). (c) R. West, P. A. Carney, and I. C. Mimco, *ibid.*, **81**, 3788 (1965). (d) G. A. Gornowicz and R. West, *ibid.*, **93**, 1714 (1971). (e) W. Priester, R. West, and T. L. Chwang, *ibid.*, **98**, 8413 (1976).

(5) (a) A. F. Halasa and D. P. Tate, *J. Organomet. Chem.*, **24**, 796 (1970). (b) A. F. Halasa and D. P. Tate, *ibid.*, **31**, 369 (1971). (c) M. D. Raush and D. J. Ciappennelli, *ibid.*, **10**, 127 (1967). (d) J. Klein and A. Medlik-Balan, *J. Am. Chem. Soc.*, **99**, 1473 (1979). (e) J. Klein and A. Medlick-Balan, *Tetrahedron Lett.*, 279 (1978).

(6) P. Krohmer and J. Goubeau, *Chem. Ber.*, **104**, 1347 (1971).

(7) F. J. Landro, J. W. Chinn, Jr., J. A. Gurak, and R. J. Lagow, *J. Am. Chem. Soc.*, in press.