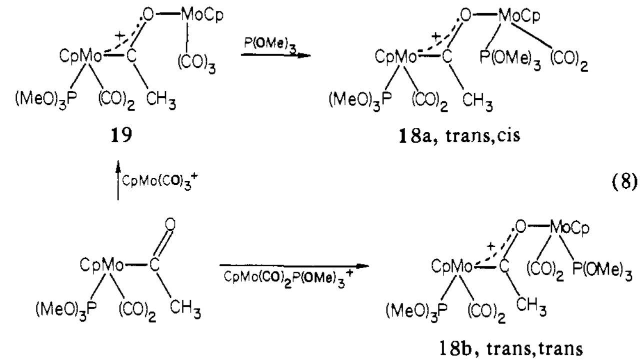
J. Am. Chem. Soc. 1982, 104, 2314-2316



(8)

Treatment of CpMo(CO)$_2$[P(OMe)$_3$]COCH$_3$ with CpMo(CO)$_2$P(OMe)$_3^+$ at −20 °C stereoselectively furnished *trans*,*trans*-**18b**[9] (71% yield) as an orange solid after ether precipitation. Stereochemical assignments resulted from established IR and $^1$H NMR correlations;[19] spectroscopically distinctive **18a** and **18b** evidently do not interconvert at room temperature. Results of I$^-$ cleavage reactions further corroborated stereochemical assignments: **18a** gave *cis*-CpMo(CO)$_2$P(OMe)$_3$I and **18b** formed *trans*-CpMo(CO)$_2$P(OMe)$_3$I, in addition to *trans*-CpMo(CO)$_2$P(OMe)$_3$(COCH$_3$), as the initial products.

**Acknowledgment.** Support from the Department of Energy, Office of Basic Energy Sciences, is gratefully acknowledged.

**Registry No. 1a**, 12108-22-4; **1b**, 12101-02-9; **2**, 64666-36-0; **3**, 81141-37-9; **4**, 68868-80-4; **5**, 81141-36-8; **6a**, 81141-29-9; **6b**, 81132-99-2; **7a**, 81133-01-9; **7b**, 81133-03-1; **8**, 81133-05-3; **9**, 81133-07-5; **10**, 12080-06-7; **11**, 12082-25-6; **12**, 12082-27-8; **13**, 81133-09-7; **14**, 81133-11-1; **15**, 81133-13-3; **17**, 56731-33-0; **18a**, 81132-96-9; **18b**, 81177-17-5; **19**, 81141-27-7; [CpFe(CO)$_3$]PF$_6$, 38834-26-3; CpMo(CO)$_3$I, 12287-61-5; CpMo(CO)$_2$I$_2^-$, 52418-55-0; CpMo(CO)$_2$(P(OMe)$_3$)COCH$_3$, 12110-00-8; [CpMo(CO)$_2$P(OMe)$_3$]PF$_6$, 81141-35-7.

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(19) (a) Barnett, K. W.; Slocum, D. W. *J. Organomet. Chem.* **1972**, *44*, 1. Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852. Trans configuration of the Mo–C (acetyl) center is consistent with thermodynamic preference for trans orientation in analogous phosphine and phosphite-substituted acyl[20b] and cationic 2-oxacyclopentylidene complexes:[20c] (b) Craig, P. J.; Green, M. *J. Chem. Soc. A* **1969**, *157*; **1968**, 1978. Craig, P. J.; Edwards, J. *J. Organomet. Chem.* **1972**, *46*, 335. (c) Cotton, F. A.; Lukehart, C. *J. Am. Chem. Soc.* **1971**, *93*, 2672; **1973**, *95*, 3552.

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## Synthetic Approaches to Coordinatively Unsaturated Heterobimetallic Complexes

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*Received October 15, 1981*

The design and synthesis of coordination compounds that contain two different metal ions are priority goals of contemporary inorganic chemistry.[1] One of the most challenging objectives of such research is the preparation of coordinatively unsaturated heterobimetallic complexes.[2] With this in mind we have examined the coordination chemistry of the recently reported chelating agent [*o*-(diphenylphosphino)benzoyl]pinacolone (HacacP).[3] This compartmentalized ligand possesses electronically dissimilar metal binding sites that facilitate the assembly of a variety of novel compounds containing both "hard" and "soft" metals.[4]

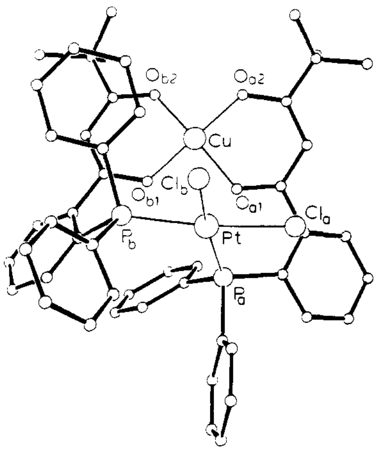
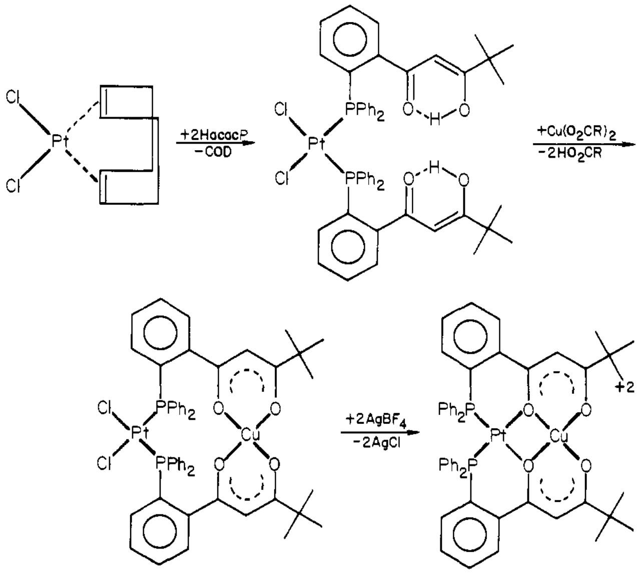


**Figure 1.** ORTEP plot for the nonhydrogen atoms of the PtCl$_2$[Cu(acacP)$_2$] molecule. For purposes of clarity, metal atoms are represented by large open circles, chlorine and phosphorus atoms by medium-sized open circles, and carbon and oxygen atoms by small open circles.

Scheme I



Red, crystalline Ir(acacP)(COD)[5] (COD = 1,5-cyclooctadiene) was readily prepared from the reaction of KacacP (generated from HacacP and KO-*t*-Bu) with [IrCl(COD)]$_2$ in THF. Its $^{31}$P NMR chemical shift of 24 ppm downfield from 85% H$_3$PO$_4$ and an intense IR band at 1665 cm$^{-1}$ indicate that here the acacP moiety functions as a PO chelating agent with a pendant $\alpha,\beta$-unsaturated ketone substituent. Mild (25 °C, 1 atm, 5 min) displacement of the COD with carbon monoxide resulted in an abrupt color change to yellow, a high-field shift in the $^{31}$P NMR spectrum, and the disappearance of the 1665-cm$^{-1}$ band in the IR spectrum. The CO stretching frequencies of the carbonylated Ir(acacP) derivative are virtually identical with those for Ir(acac)(CO)$_2$,[6,7] consistent with the binding of the Ir(CO)$_2$ moiety by the O···O site of the

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(1) Lindvedt, R. L.; Tomlonovic, B.; Fenton, D. E.; Glick, M. D. *Adv. Chem. Ser.* **1976**, *150*, 407. Glick, M. D.; Lindvedt, R. L. *Prog. Inorg. Chem.* **1976**, *21*, 233. Casellato, U.; Vigato, P. A.; Fenton, D. E.; Bidali, M. *Chem. Soc. Rev.* **1979**, *8*, 199.

(2) Stremple, P.; Bainziger, N. C.; Coucouvanis, D. *J. Am. Chem. Soc.* **1981**, *103*, 4601. Gunter, M. J.; Mander, L. N.; Murray, K. S. *J. Chem. Soc., Chem. Commun.* **1981**, 799.

(3) Rauchfuss, T. B.; Wilson, S. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 6769. See also: Wrobleski, D. A.; Wilson, S. R.; Rauchfuss, T. B. *Inorg. Chem.*, in press.

(4) 2-(Diphenylphosphino)pyridine is a hard–soft binucleating ligand which, in contrast to acacP, binds in a head-to-tail manner in its heterobimetallic complexes: Farr, J. P.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 6654.

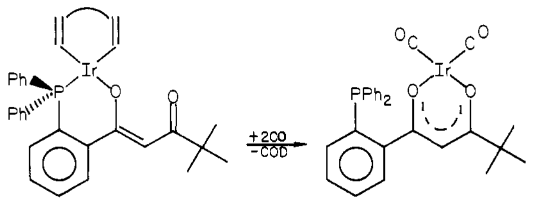
(5) All new compounds described in this paper analyze satisfactorily for the elements indicated. Anal. C, H; IR (mull) 1665 (s), 1610 (m) cm$^{-1}$; $^1$H NMR (90 MHz, CDCl$_3$) $\delta$ 8.0–7.0 (m, 14 H), 5.7 (d, 1 H), 3.7 (m, 4 H), 1.8 (m, 8 H), 0.8 (s, 9 H); $^{31}$P{$^1$H} NMR (40.5 MHz, CD$_2$Cl$_2$) +24.0 ppm (downfield from 85% H$_3$PO$_4$); UV–vis (CH$_2$Cl$_2$) 555 nm (446 cm$^{-1}$ M$^{-1}$), 472 nm (2530 cm$^{-1}$ M$^{-1}$), 396 nm (1600 cm$^{-1}$ M$^{-1}$).

(6) IR (mull) 2070 (vs), 1998 (vs) cm$^{-1}$; $^{31}$P{$^1$H} NMR (40.5 MHz, CD$_3$Cl$_2$) −2.2 ppm; UV–vis (CH$_2$Cl$_2$) 408 nm (2260 cm$^{-1}$ M$^{-1}$).

(7) Bonati, F.; Ugo, R. *J. Organomet. Chem.* **1968**, *11*, 341.

0002-7863/82/1504-2314$01.25/0

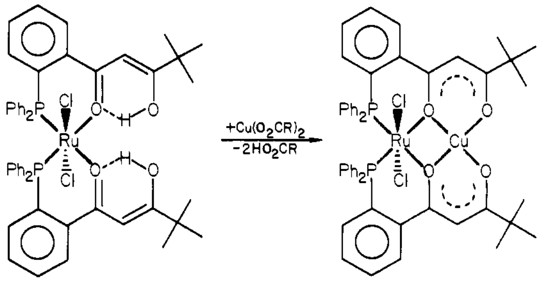
acacP ligand (eq 1). These experiments establish the dependence of the site selectivity of acacP on the $\pi$ basicity of the metal ion.



(1)

Following the reaction sequence outlined in Scheme I, the 1,5-cyclooctadiene complexes $MCl_2(COD)$ (M = Pt, Pd) were quantitatively converted to their HacacP derivatives $MCl_2(HacacP)_2$.[8,9] Both the cream-colored platinum and the yellow palladium HacacP complexes react efficiently with cupric carboxylates to afford emerald green paramagnetic heterobimetallic derivatives, *cis*-$MCl_2[Cu(acacP)_2]$.[10,11] These compounds exhibit spectroscopic features characteristic of the copper(II)bis(diketonate) and *cis*-$MCl_2(PR_3)_2$ centers. The molecular structure of $PtCl_2[Cu(acacP)_2]$ as elucidated by single-crystal X-ray diffraction methods[13] is shown in Figure 1. The molecule is composed of nearly square-planar platinum ($PtCl_2P_2$ coplanar to within 0.12 Å) and copper ($CuO_4$ coplanar to within 0.21 Å) subunits covalently linked by the flexible acacP backbone. The coordination geometry of the platinum center, presumably like its precursor, consists of the familiar *cis*-$PtCl_2(PR_3)_2$ arrangement. The cupric ion is accommodated by the $O_4$ site provided by the two acacP ligands. The angle between the least-squares mean planes for the $PtCl_2P_2$ and $CuO_4$ groups is 67.5°. The copper–platinum separation of 3.966 (1) Å is nonbonding but geometrically suitable for the binding of small substrates. The structure also shows that compounds of the type *cis*-$ML_n(HacacP)_2$ are effective tetradentate chelating agents despite the fact that their transformation to such bimetallic derivatives involves the formation of a 12-membered ring.[14] Addition of $AgBF_4$ (2 equiv) to a THF solution of $PtCl_2[Cu(acacP)_2]$ gave the lime green cationic complex $[PtCu(acacP)_2](BF_4)_2$.[15]

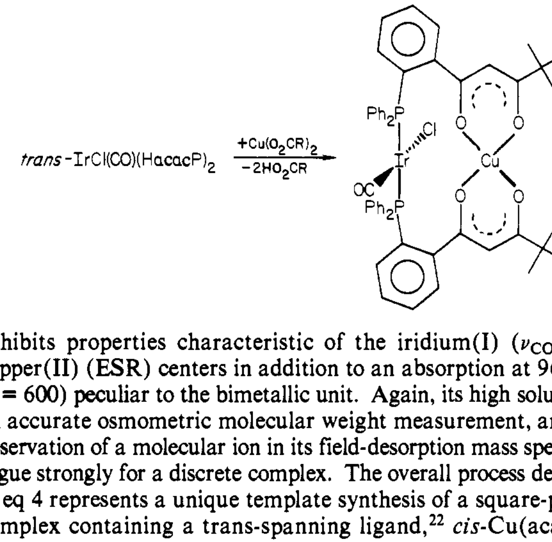
We have previously established that many ortho-substituted triarylphosphines efficiently react with $RuCl_2(PPh_3)_3$ to give complexes of the type *trans,cis,cis*-$RuCl_2(o\text{-}Ph_2PC_6H_4X)_2$ where X = $OCH_3$, CHO, and $C(O)CH_3$.[16,17] Using this approach, we prepared $RuCl_2(HacacP)_2$,[18] a sparingly soluble blue compound which reacted cleanly with cupric acetate to give the red heterobimetallic complex $RuCl_2[Cu(acacP)_2]$[19] (eq 2). The high solubility of this bimetallic derivative in nonpolar organic solvents indicated a discrete species, a fact supported by field-desorption mass spectrometry and an osmometric molecular weight determination. Its electronic absorption spectrum is not the sum of the spectra of green $Cu(PhCOCHCOC(CH_3)_3)_2$ and $RuCl_2(HacacP)_2$ but more closely resembles that for $RuCl_2(o\text{-}Ph_2PC_6H_4OCH_3)_2$.[17]



(2)

The third synthesis of an acacP bridged bimetallic complex started with the preparation of *trans*-$IrCl(CO)(HacacP)_2$[20] (eq 3), a yellow crystalline compound which is strictly analogous to *trans*-$IrCl(CO)(PPh_3)_2$. Reaction of our iridium(I) complex with cupric carboxylates cleanly gave *red* crystalline *trans*-$IrCl(CO)[Cu(acacP)_2]$[21] (eq 4). This novel bimetallic derivative exhibits properties characteristic of the iridium(I) ($\nu_{CO}$) and copper(II) (ESR) centers in addition to an absorption at 960 nm ($\epsilon$ = 600) peculiar to the bimetallic unit. Again, its high solubility, an accurate osmometric molecular weight measurement, and the observation of a molecular ion in its field-desorption mass spectrum argue strongly for a discrete complex. The overall process depicted in eq 4 represents a unique template synthesis of a square-planar complex containing a trans-spanning ligand,[22] *cis*-$Cu(acacP)_2$. Another important characteristic of *trans*-$IrCl(CO)[Cu(acacP)_2]$ is that the iridium(I) center retains its ability to undergo reactions

$$IrCl(CO)_2(p\text{-}H_2NC_6H_4Me) \xrightarrow[-H_2NC_6H_4Me,CO]{+2HacacP} trans\text{-}IrCl(CO)(HacacP)_2 \quad (3)$$



(4)

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(8) Anal. C, H, Cl, P; IR (mull) 1595 (s) cm$^{-1}$; $^{31}P\{^1H\}$ NMR (40.5 MHz, $CD_2Cl_2$) +15.2 ppm ($^1J_{^{195}Pt,^{31}P}$ = 4187 Hz); UV-vis ($C_6H_6$) 295 nm (1.9 × $10^4$ cm$^{-1}$ M$^{-1}$).

(9) Anal. C, H, Cl; IR (mull) 1602 (s) cm$^{-1}$; $^1H$ NMR (90 MHz, $CDCl_3$) $\delta$ 8.0–7.1 (m, 14 H), 6.1 (s, 1 H), 1.2 (s, 9 H).

(10) Anal. C, H, Cu, P; IR (mull) 1572 (m), 1550 (s), 1518 (s) cm$^{-1}$; ESR (frozen $CH_2Cl_2$, −196 °C) $g_{\parallel}$ = 2.32, $A_{\parallel}$ = 1.77 × $10^{-2}$ cm$^{-1}$; UV-vis ($C_6H_6$) 676 nm (170 cm$^{-1}$ M$^{-1}$), 316 nm (1.9 × $10^4$ cm$^{-1}$ M$^{-1}$); FDMS, $m/z$ 1068 ((M − Cl)$^+$), 1033 ((M − $Cl_2$)$^+$).

(11) Anal. C, H, Cl, Cu, P; IR (mull) 1605 (w), 1570 (m), 1545 (s), 1515(s) cm$^{-1}$; ESR (frozen $CH_2Cl_2$, −196 °C) $g_{\parallel}$ = 2.27, $A_{\parallel}$ = 1.90 × $10^{-2}$ cm$^{-1}$; UV–vis ($C_6H_6$) 740 nm (280 cm$^{-1}$ M$^{-1}$), 336 (3.0 × $10_4$ cm$^{-1}$ M$^{-1}$); FAB MS,[12] $m/z$ 945 ((M–$Cl_2$)$^+$).

(12) Fast-atom bombardment mass spectroscopy (FAB MS): Barber, M.; Bordoli, R. S.; Sedgwick, R. D.; Tyler, A. N. *J. Chem. Soc., Chem. Commun.* **1981**, 325.

(13) Crystallographic analysis was performed by Dr. C. S. Day of Crystalytics Co. The single cube-shaped crystal, 0.75 mm on edge, of $PtCl_2[Cu(acacP)_2]\cdot 2CH_2Cl_2\cdot H_2O$ was triclinic, space group $P\bar{1}$—$C_i^1$ (No. 2) with $a$ = 11.914 (6), $b$ = 11.646 (6), $c$ = 21.125 (10) Å; $\alpha$ = 102.34 (4), $\beta$ = 103.71 (4), $\gamma$ = 99.83 (4)°; $V$ = 2705 (2) Å$^3$, $Z$ = 2. Three-dimensional X-ray diffraction data were collected for 12 435 independent reflections having $3 \geq 2\theta \geq 55°$ on a computer-controlled four-circle Nicolet autodiffractometer using graphite monochromated Mo K$\bar{\alpha}$ radiation ($\lambda$ = 0.71073 Å) and 1.10°-wide $\omega$ scans. The structure was solved by using the heavy-atom technique, and the resulting nonhydrogen atoms have been refined anisotropically to convergence ($R$ = 0.053 and $R_w$ = 0.065 for 8881 independent reflections having $I > 3\sigma(I)$ and $2\theta_{MoK\bar{\alpha}} \leq 55°$) by using empirically weighted least-squares techniques on a Data General Eclipse S-200 computer. The function minimized was $\sum w||F_o| - |F_c||^2$, $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$. Full experimental details are included in the supplementary material and will be described in the full paper: Day, C. S.; Rauchfuss, T. B.; Wrobleski, D. A., to be submitted for publication.

(14) Other metal complexes of chelating bis($\beta$-diketonates) have been described: Ito, Y.; Sugaya, T.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1977**, *99*, 8366.

(15) Anal. C, H, Cu, P; IR (mull) 1622 (s), 1597 (s), 1562 (w), 1510 (s), 1050 (vs) cm$^{-1}$; ESR (frozen $CH_2Cl_2$, −196 °C) $g_{\parallel}$ = 2.32, $A_{\parallel}$ = 1.62 × $10^{-2}$ cm$^{-1}$.

(16) Rauchfuss, T. B. *J. Am. Chem. Soc.* **1979**, *101*, 1045. Cirrincione, C.; Rauchfuss, T. B.; Wrobleski, D. A., to be submitted for publication.

(17) Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1979**, *18*, 2658.

(18) Anal. C, H, Cl, P; IR (mull) 1590 (s), 1565 (s), 1520 (m) cm$^{-1}$; UV–vis ($C_6H_6$) 560 nm (4.0 × $10^3$ cm$^{-1}$ M$^{-1}$), 321 nm (2.9 × $10^4$ cm$^{-1}$ M$^{-1}$).

(19) Anal. C, H, Cu, P; IR (mull) 1570 (m), 1549 (m), 1500 (s) cm$^{-1}$; ESR (frozen $CH_2Cl_2$, −196 °C) $g_{\parallel}$ = 2.30, $A_{\parallel}$ = 1.60 × $10^{-2}$ cm$^{-1}$; UV–vis ($C_6H_6$) 704 nm (140 cm$^{-1}$) 513 nm (1.8 × $10^3$ cm$^{-1}$ M$^{-1}$), 428 nm (3.2 × $10^3$ cm$^{-1}$ M$^{-1}$), 322 nm (2.7 × $10^4$ cm$^{-1}$ M$^{-1}$).

(20) Anal. C, H, Cl, P; IR (mull) 1957 (vs), 1601 (s), 1585 (s), 1560 (m) cm$^{-1}$; $^{31}P\{^1H\}$ NMR (40.5 MHz, $CD_2Cl_2$) +26.8 ppm (w), +25.9 ppm (w), +24.9 ppm (vs); UV–vis ($C_6H_6$) 432 nm (670 cm$^{-1}$ M$^{-1}$), 384 nm (3.4 × $10^3$ cm$^{-1}$ M$^{-1}$), 290 nm (2.4 × $10^4$ cm$^{-1}$ M$^{-1}$).

(21) Anal. C, H, Cl, P; IR (mull) 1970 (vs), 1978 (vs), 1589 (s), 1558 (m), 1500 (s), cm$^{-1}$; ESR (frozen $CH_2Cl_2$, −196 °C) $g_{av}$ = 2.14; UV–vis ($C_6H_6$) 960 nm (600 cm$^{-1}$ M$^{-1}$), 533 nm (250 cm$^{-1}$ M$^{-1}$), 433 nm (2.4 × $10^3$ cm$^{-1}$ M$^{-1}$), 341 nm (2.0 × $10^4$ cm$^{-1}$ M$^{-1}$).

(22) Mochida, I.; Mattern, J. A.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 3021 and references therein.

with substrates such as sulfur dioxide (reversibly), hydrogen chloride, and methyl iodide, although unlike *trans*-IrCl(CO)(PPh$_3$)$_2$ it does not bind molecular oxygen.

**Acknowledgment.** This research was supported by Dow Chemical Co. FD and FAB mass spectra were obtained in the Mass Spectrometry Laboratory, which is supported by a grant from the National Institute of General Medical Sciences (GM 27029).

**Registry No.** *cis*-PtCl$_2$[Cu(acacP)$_2$], 81141-51-7; *cis*-PdCl$_2$[Cu(acacP)$_2$], 81141-52-8; PtCl$_2$(HacacP)$_2$, 81141-53-9; PdCl$_2$(HacacP)$_2$, 81141-54-0; Ir(acacP)(CO)$_2$, 81141-55-1; Ir(acacP)(COD), 81141-56-2; [PtCu(acacP)$_2$](BF$_4$)$_2$, 81141-58-4; RuCl$_2$(HacacP)$_2$, 81157-61-1; RuCl$_2$[Cu(acacP)$_2$], 81141-59-5; *trans*-IrCl(CO)(HacacP)$_2$, 81157-62-2; *trans*-IrCl(CO)[Cu(acacP)$_2$], 81141-60-8; [IrCl(COD)]$_2$, 12112-67-3; PtCl$_2$(COD), 12080-32-9; PdCl$_2$(COD), 12107-56-1; RuCl$_2$(PPh$_3$)$_3$, 15527-49-4; IrCl(CO)$_2$(*p*-H$_2$NC$_6$H$_4$Me), 59952-74-8.

**Supplementary Material Available:** Tables of structure factors, positional parameters, thermal parameters, angles, distances, and a complete structural report for Cl$_2$Pt[Cu(acacP)$_2$] (51 pages). Ordering information is given on any current masthead page.

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# Synthesis and Molecular Structure of a Transition-Metal Cyclamphosphoranide. A Pentacyclic Structure with the Metal Bridging a P-N Bond

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Cyclamphosphorane **1** and related compounds[1] have recently given rise to considerable interest. Their polycyclic structures engender original behavior: they have led to phosphonium ions that undergo a remarkable dimerization,[2] to the first P(V)-P(V) compound, dicyclendiphosphorane,[3] to the first phosphonium salts containing ionic fluoride,[4] under X-ray irradiation to a phosphoranyl radical[5] remarkably stereodynamic in the solid, etc. We now report the displacement of the tautomeric equilibrium **1** under the action of a transition-metal derivative and the easy formation of stable transition-metal phosphoranides.

The first transition-metal phosphoranides, i.e., compounds in which a 4-connected phosphoranide anion, **2**, acts as a donor ligand toward a transition metal, have recently been obtained from bicyclic aminophosphoranes.[6,7] The tetracyclic structure of **1** appears to convey additional stability to such phosphoranide adducts.

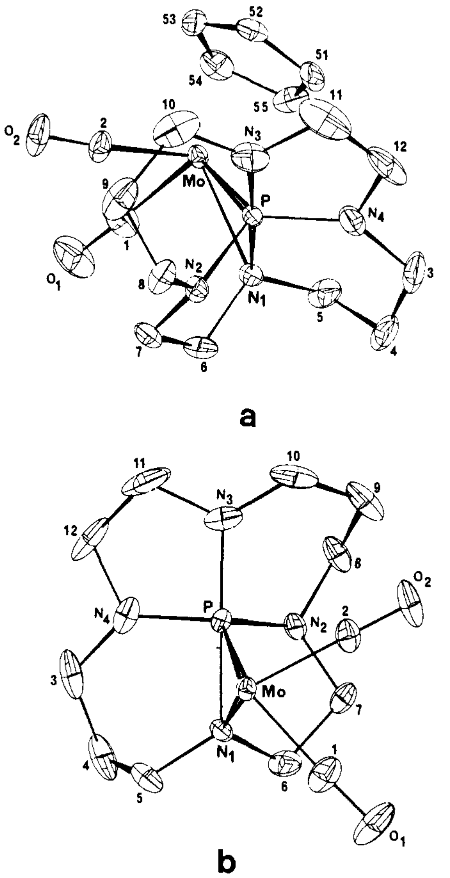

**Figure 1.** (a) ORTEP diagram showing the trigonal bipyramidal arrangement of the bonds on phosphorus. (b) View of the NMoP bridge and pentacyclic structure. The $\eta^5$-C$_5$H$_5$ ring has been omitted in **1b** for clarity. Selected bond lengths, Å (and standard deviations): P-Mo, 2.444 (2); P-N$_1$, 1.854 (5); P-N$_2$, 1.697 (6); P-N$_3$, 1.696 (7); P-N$_4$, 1.670 (7); N$_1$-Mo, 2.223 (5). Angles (°); MoPN$_1$, 60.5 (2); MoPN$_2$, 116.4 (2); MoPN$_3$, 116.2 (2); MoPN$_4$, 118.0 (2); N$_1$PN$_3$, 176.6 (3); N$_2$PN$_4$, 117.6 (3); N$_1$PN$_4$, 93.8 (3); N$_1$PN$_2$, 87.8 (3); N$_2$PN$_3$, 93.5 (3); N$_3$PN$_4$, 88.4 (4).

Solutions of cyclamphosphorane have been shown by Atkins and Richman to consist of an equilibrated mixture of the closed (**1a**) and open (**1b**) tautomers. When this mixture is allowed to react with ($\eta^5$-C$_5$H$_5$)Mo(CO)$_3$Cl,[8] the equilibrium is quantitatively shifted to the right, with formation of a mixture of adducts **3** and **4**, in which the open cyclamphosphane form behaves either as a monodentate (through P) or a bidentate (through P and one N) *ligand* toward the transition metal. Compounds **3** and **4** are characterized[9] in the mixture by two signals in the $^{31}$P NMR spectrum at 144.6 and 149.8 ppm, with respective peak areas of 25% and 75%.[10] Conductimetric measurements in acetone solutions are consistent with the presence of ca. 20% of an ionic species. Only the ionic constituent of the reaction mixture appears to undergo nucleophilic attack under the action of LiMe to give the phosphoranide **6**. Formulations **3** + **4** are further asserted by their quantitative conversion to **5** under the action of NaBPh$_4$. Compound **5** arises as two diastereoisomers ($\delta$ ($^{31}$P) +144.8; $\delta$ ($^1$H$_{Cp(1)}$) 5.60, $\delta$ ($^1$H$_{Cp(2)}$) 5.73 in a 17:83 ratio).

The molybdenum cyclamphosphoranide **6** was obtained in over 90% yield when a THF solution of **5** was treated with 1 equiv of LiMe for 1 h at room temperature. It occurs as yellow-orange crystals, moderately air sensitive, soluble in THF and CHCl$_3$, and

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[†] Member of the Université Scientifique et Médicale de Grenoble, Laboratoire Associé au CNRS N° 321.

(1) Richman, J. E. *Tetrahedron Lett.* **1977**, 559. Atkins, T. J.; Richman, J. E. *Tetrahedron Lett.* **1978**, 5149.

(2) Richman, J. E.; Gupta, O. D.; Flay, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 1291.

(3) Richman, J. E.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 3955. Richman, J. E.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1981**, *20*, 3378.

(4) Richman, J. E.; Flay, R. B. *J. Am. Chem. Soc.* **1981**, *103*, 5265.

(5) Hamerlinck, J. H. H.; Hermkens, P. H. H.; Schipper, P.; Buck, H. M. *J. Chem. Soc., Chem. Comm.* **1981**, 358.

(6) Jeanneaux, F.; Grand, A.; Riess, J. G. *J. Am. Chem. Soc.* **1981**, *103*, 4272.

(7) Wachter, J.; Mentzen, B. F.; Riess, J. G. *Angew. Chem.* **1981**, *93*, 299.

(8) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

(9) See also: Wachter, J.; Jeanneaux, F.; Riess, J. G. *Inorg. Chem.* **1980**, *19*, 2169.

(10) The Cp ring exhibits four singlets in the $^1$H NMR spectrum (5.54 (48%), 5.59 (22%), 5.79 (22%), 5.83 (7%) ppm), which is consistent with the possibility of having two diastereomers for both **3** and **4**.