Inorganica Chimica Acta
LETTER

The preparation of heterobimetallic complexes using a new heterodifunctional ligand system: X-ray structural analysis of $(CO)_3Cr\text{-}\eta^6[C_6H_5CH_2\overline{P(Ph)\text{-}CH_2CH_2CH_2PCy_2}PtMe_2]$

Mark G. McDougall*, Judith C. Gallucci
and Devon W. Meek†
Department of Chemistry, Ohio State University,
Columbus, OH 43210 (U.S.A.)

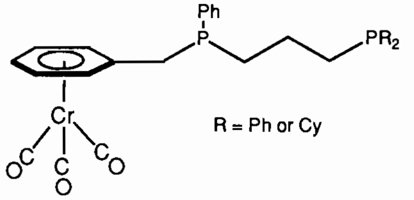
(Received June 24, 1991)

The design and synthesis of ligation systems which preferentially tether two or more different metals together into a single molecule has been growing for the past decade [1]. The potential exists for a number of novel small molecule transformations to occur on metals centers of dissimilar reactivity which are held in close proximity to each other. Initially, we study a template in which a late transition metal enjoys the stability of bidentate ligation in the presence of an early transition metal still capable of metal-centered chemistry.

The stepwise construction of our heterodifunctional mixed-metal compounds began with the synthesis of a chromium tricarbonyl-bound arene bearing a free pendent bisphosphine ligand according to eqns. (1) and (2).

$$PhCH_2OH + Cr(CO)_6 \xrightarrow[\Delta]{DME} (CO)_3Cr\text{-}\eta^6[PhCH_2OH] \xrightarrow[-H_2O]{HCl / C_6H_6} (CO)_3Cr\text{-}\eta^6[PhCH_2Cl] \qquad (1)$$

$$(CO)_3Cr\text{-}\eta^6[PhCH_2Cl] + LiP(Ph)(CH_2)_3PR_2 \xrightarrow{THF}$$



(2)

Chromium tricarbonyl metallation of benzyl alcohol was accomplished according to the method of Pittman *et al.* [2], and followed by benzylic chlorination using a modification of the procedure of Pettit and coworkers [3]. The lithium salt of either $HP(Ph)CH_2CH_2CH_2PPh_2$ [4] or $HP(Ph)CH_2CH_2CH_2PCy_2$ [5], generated with n-BuLi in THF, was added to the benzyl chloride derivative generating $(CO)_3Cr\text{-}\eta^6[C_6H_5CH_2P(Ph)CH_2CH_2CH_2PR_2]$ as orange oils in up to 95% yield (where R = Ph, CrPP and R = Cy, CrPPCy). The ^{31}P NMR assignments are listed in Table 1. The IR carbonyl-stretching frequencies in CH_2Cl_2 are 1978 and 1900 cm^{-1} for CrPP, and 1976 and 1901 cm^{-1} for CrPPCy. One notable feature of the ^1H NMR appears in the region of the arene complexed by chromium (4.6–5.3 ppm). Each individual proton of the ring has a unique chemical shift environment. These protons, four to five bonds removed from the chiral phosphine center, display larger chemical shift differences than the methylene protons, which appear as a simple doublet (2.61 ppm, CrPP; 2.59 ppm, CrPPCy). Non-equivalence may be due either to intrinsic asymmetry pronounced by chromium mediated magnetic anisotropy or preferential conformation of the arene ring with respect to the rest of the molecule.

The addition of either CrPP or CrPPCy to $[PtMe_2(COD)]$ with stirring in benzene causes the precipitation of a light yellow solid over a period of 15 min. The compounds $(CO)_3Cr\text{-}\eta^6[C_6H_5CH_2\overline{P(Ph)CH_2CH_2CH_2PR_2}PtMe_2]$ (R = Ph, CrPPPtMe$_2$

TABLE 1. $^{31}Pt\{^1H\}$ NMR data for the Cr(0) ligands and Cr(0)–Pt(II) complexes

Complex	Assignment[a]		
	Ph_2P–	Cy_2P–	$(CO)_3CrBz(Ph)P$–
CrPP	–17.7		–16.5
CrPPCy		–7.7	–17.2
CrPPPtMe$_2$	1.2[b]		4.2[b]
^1J(Pt–P) (Hz)	1791		1846
CrPPCyPtMe$_2$		4.6[c]	4.0[c]
^1J(Pt–P) (Hz)		1812	1902

[a] Chemical shifts are in ppm relative to external H_3PO_4. [b] ^2J(P–P) = 16.5 Hz. [c] ^2J(P–P) = 18.4 Hz.

---

*Author to whom correspondence should be addressed. Present address: NCI-Frederick Cancer Research and Development Center, ABL-Basic Research Program, Frederick, MD 21701, U.S.A.

†Deceased.

0020-1693/91/$3.50

© 1991 — Elsevier Sequoia, Lausanne

and R = Cy, CrPPCyPtMe$_2$) are obtained in a 79% and 75% yield, respectively, after washing in petroleum ether and drying *in vacuo*. The ^{31}P NMR spectra of the two new compounds are listed in Table 1. Assignments have been made on the basis of two-dimensional NMR ^{31}P{^{1}H} correlation spectra. Within each complex, the phosphine containing the chromium tricarbonyl bound benzylic substituent displays the larger ^1J(P–Pt) coupling constant of the two phosphine donors. In general, as the size of substituents on phosphorus is increased, there is a relative decrease in the bond order of that donor, and similarly in the one-bond metal–phosphorus coupling constant [6]. Therefore, the bulky metal bound benzylic substituent is thought to assume a conformation which limits non-bonding steric interactions because the phosphine donor to which it is attached exhibits relatively stronger binding to the metal center. The IR carbonyl-stretching frequencies for CrPPPtMe$_2$ are 1968 and 1890 cm^{-1} and for CrPPCyPtMe$_2$ are 1970 and 1892 cm^{-1}, both recorded in CH$_2$Cl$_2$. These values show little change from those of the starting materials and clearly indicate that no substantial electronic or steric effects perturb the Cr(CO)$_3$ group upon complexation with platinum. The ^{1}H NMR spectra again reveal magnetic non-equivalency for each proton of the metal bound arene ring. The benzylic methylene proton absorptions, however, become anisochronous upon phosphorus complexation (CrPPPtMe$_2$: 3.40 ppm (dd) ^2J(P–H) = 8.1, ^2J(H–H) = 10.4, ^3J(Pt–H) = 7 Hz; 3.10 ppm (dd) ^2J(P–H) = 13.9, ^2J(H–H) = 10.4, ^3J(Pt–H) = 40 Hz; CrPPCyPtMe$_2$: 3.42 ppm (dd) ^2J(P–H) = 7, ^2J(H–H) = 7, ^3J(Pt–H) = 7 Hz; 3.00 ppm (dd) ^2J(P–H) = 11.2, ^2J(H–H) = 7.0, ^3J(Pt–H) = 39.8 Hz). Non-equivalence of diastereotopic benzylic protons is dependent on steric factors [7], but does not necessarily exhibit large chemical shift differences when attached to phosphines bound to Group 10 metals [8]. The non-equivalency of the protons in these complexes does not change over a temperature range of −35 to 100 °C.

To confirm the nature of the bimetallic structure of the complex CrPPCyPtMe$_2$ in the solid state, an X-ray structure determination was undertaken on a Syntex (Nicolet) P1 diffractometer equipped with Mo Kα radiation. Crystal data for CrPPCyPtMe$_2$ are as follows: monoclinic, space group $P2_1/c$, a = 10.209(2), b = 16.561(4), c = 19.896(4) Å, β = 101.95(2), V = 3291 Å^3, Z = 4, D_c = 1.61 g/cm^3, μ = 47.4 cm^{-1}, T = 293 K. The data ($4° \leqslant 2\theta \leqslant 50°$) were corrected for Lorentz and polarization effects, a small amount of decay (6% based on intensity), and absorption. The structure was solved by a combination of the Patterson method and the direct methods program DIRDIF [9] and refined by full-matrix least-squares (SHELX-76 [10]) using the 4125 unique reflections with $I > 3\sigma(I)$. The final refinement cycles included anisotropic thermal parameters for the non-hydrogen atoms with hydrogen atoms fixed at idealized positions (C–H = 0.98 Å and B(H) = B_{iso} (C) + 1.0 Å^2) and resulted in agreement indices of $R(F)$ = 0.030 and $R_w(F)$ = 0.030 for the 361 variables. Scattering factors for the P, O, C and H atoms were used as supplied by SHELX-76 [10]; scattering factors for the Pt and Cr atoms were obtained from ref. 11; they include anomalous dispersion terms.

Select bond distances and angles are given in Table 2 and the labeling scheme is shown in the ORTEP drawing of Fig. 1. The platinum atom is situated in the center of an approximately planar arrangement. The methyl groups are held in a *cis* position as required by the geometry of the bidentate diphosphine ligand. The P–Pt–P angle of 95.95(6)° is larger than ideal for a square planar geometry. This is not surprising in view of the large steric requirements imposed by the dicyclohexyl and chromium bound benzyl substituents. The Pt–P bond lengths of the solid state correlate with the solution ^1J(Pt–P) coupling constants, in that the shorter bond yields the larger coupling. The arene bound by chromium tricarbonyl is situated towards the platinum metal center. No direct metal–metal interaction is observed (Pt····Cr distance is 5.658 Å). The *ortho* position (C26) sits above the Pt–C5 bond at an arene hydrogen-to-methyl hydrogen distance of 2.81 Å. No platinum coupling in the solution NMR spectra is observed for this *ortho* position. Nonetheless, a non-bonding

TABLE 2. Selected final bond lengths and angles for the structure of CrPPCyMe

	Bond length (Å)		Bond angle (°)
Pt–P1	2.288(2)[a]	P1–Pt–P2	95.95(6)
Pt–P2	2.250(2)	P1–Pt–C4	91.2(2)
Pt–C4	2.130(5)	P1–Pt–C5	175.0(2)
Pt–C5	2.162(6)	P2–Pt–C4	172.3(2)
P1–C1	1.847(6)	P2–Pt–C5	89.1(2)
C1–C2	1.490(9)	C4–Pt–C5	83.7(2)
P1–C6	1.844(6)	Pt–P1–C1	117.0(2)
P1–C12	1.845(6)	Pt–P1–C6	113.3(2)
P2–C3	1.845(7)	Pt–P1–C12	114.6(2)
C2–C3	1.517(9)	Pt–P2–C3	119.5(2)
P2–C18	1.837(6)	Pt–P2–C18	117.1(2)
P2–C24	1.848(6)	Pt–P2–C24	112.0(2)
C24–C25	1.502(8)	P2–C24–C25	111.8(4)
Pt····Cr	5.658		
Cr····RC[b]	1.712		

[a] The values in parentheses are e.s.d.s in the least significant figure. [b] RC denotes the ring centroid of the ring composed of atoms C25, C26, C27, C28, C29 and C30.

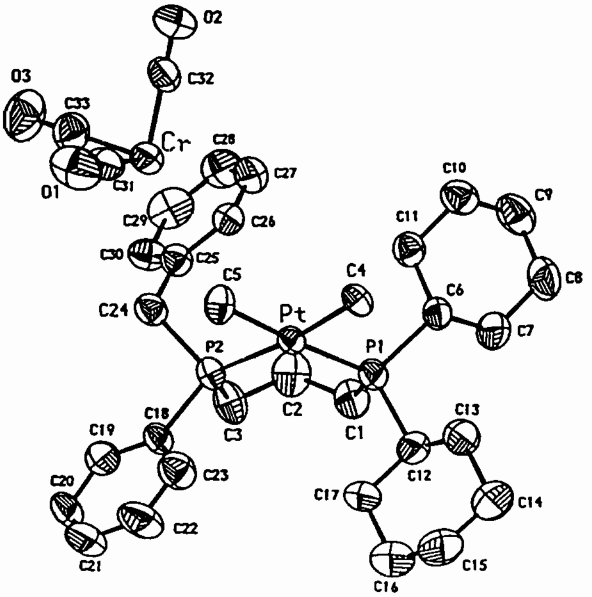


Fig. 1. An ORTEP drawing of the structure of Cr-PPCyPtMe$_2$, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

interaction arising from the proximity of the arene ring may destabilize the Pt–C5 bond. This bond is longer then its neighbor, Pt–C4, yet is *trans* to the longer Pt–P bond.

Acknowledgement

We thank the Materials Research Fund, administered by the National Science Foundation for support of this work.

References

1 J. Szymoniak, J. Besancon, A. Dormond and C. Moise, *J. Org. Chem., 55* (1990) 1429; J. K. Stille, C. Smith, O. P. Anderson and M. M. Miller, *Organometallics, 8* (1989) 1040; K. V. Katti and R. G. Cavell, *Inorg. Chem., 28* (1989) 413; G. K. Anderson and M. Lin, *Organometallics, 7* (1988) 2285; G. K. Anderson and M. Lin, *Inorg. Chim. Acta, 142* (1988) 7; G. S. White and S. W. Stephan, *Organometallics, 6* (1987) 2169.

2 C. U. Pittman, Jr., R. L. Voges and J. Elders, *Macromolecules, 4* (1971) 302.

3 J. D. Holmes, D. A. K. Jones and R. Pettit, *J. Organomet. Chem., 4* (1965) 324.

4 R. J. Uriarte, T. J. Mazenec, K. D. Tau and D. W. Meek, *Inorg. Chem., 19* (1980) 79.

5 R. Glaser, D. J. Kountz, R. D. Waid, J. C. Gallucci and D. W. Meek, *J. Am. Chem. Soc., 106* (1984) 6324.

6 C. A. Tolman, *Chem. Rev., 77* (1977) 313, and refs. therein.

7 W. R. Jackson and W. B. Jennings, *J. Chem. Soc. B,* (1969) 1221.

8 A. W. Verstuyft, D. A. Redfield, L. W. Cary and J. A. Nelson, *Inorg. Chem., 16* (1977) 2776.

9 P. T. Beurskens, W. P. Bosman, H. M. Doesburg, R. O. Gould, Th. E. M. Van den Hark, P. A. J. Prick, J. H. Noordik, G. Beurskens, V. Parthasarathi, H. J. Bruins Slot and R. C. Haltiwanger, *DIRDIF: Direct Methods for Difference Structures,* Crystallography Laboratory, University of Nijmegen, The Netherlands, 1983.

10 G. M. Sheldrick, *SHELX-76 Program for Crystal Structure Determination,* University Chemical Laboratory, Cambridge, U.K., 1976.

11 *The International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, U.K., 1974, p. 99.