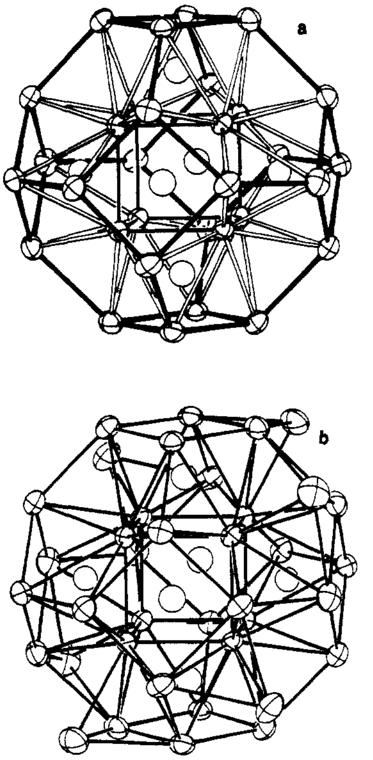

Figure 2. $Ni_{38}C_6$ metal frame (b) and the truncated-octahedral $Ni_{32}C_6$ moiety (a), which represents a fragment of the structure of $Cr_{23}C_6$ (solid lines depict the inner Ni_8 cube and the outer truncated-octahedral polyhedron; open circles represent the interstitial carbide atoms).

by the presence of strongest absorptions in the edge-bridging carbonyl stretching region.[8]

The $Ni_{32}C_6$ inner core of the $[HNi_{38}(CO)_{42}C_6]^{5-}$ cluster (Figure 2a) is closely related to a fragment of the structure of $Cr_{23}C_6$.[7] The $Cr_{23}C_6$ interstitial alloy has a $Fm3m$ structure which conforms to the No. 24 of Andreini's space-filling models[15,16] and derives from a regular sequence of $Cr_{32}C_6$ truncated octahedra of frequency 1[13] and Cr_{13} cuboctahedra three-dimensionally fused through their square faces. The truncated-octahedral $Cr_{32}C_6$ moiety has a structure identical with that shown by the $Ni_{32}C_6$ moiety of $[HNi_{38}(CO)_{42}C_6]^{5-}$ and also shows very similar molecular parameters. It is worth noting that the only well-defined Ni–C interstitial alloy, viz., Ni_3C,[2,17] shows a hexagonal close-packed nickel lattice encapsulating the carbide atoms in octahedral cavities.[18,19]

To our knowledge $[HNi_{38}(CO)_{42}C_6]^{5-}$ represents the first example of stabilization in a molecular cluster of an extended fragment of the structure of a metal–carbide alloy and is suggestive of the possibility of a molecular approach to new Ni–C binary phases.

Acknowledgment. We thank the M.P.I. (Rome) for a grant and the Centro del CNR per la Sintesi e la Struttura (Milano) for the use of equipment. Helpful discussions with Prof. A. Sironi are gratefully acknowledged.

Supplementary Material Available: Lists of atomic coordinates (Table I), thermal factors (Table II), and bond distances and angles (Table III) and a figure with labeling of $[NBu_4]_5$-$[HNi_{38}(CO)_{42}C_6]$ (36 pages). Ordering information is given on any current masthead page.

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Synthesis of Organometallic Heterodinuclear μ-Oxo Complexes by Extrusion of Alkenes from Zirconium/Tungsten Oxaalkyl Complexes

Eric N. Jacobsen, Mary K. Trost, and Robert G. Bergman*

Department of Chemistry, University of California
Berkeley, California 94720

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Because of the role they have played in structural inorganic[1] and bioinorganic chemistry,[2] many μ-oxo complexes have been prepared and studied. Nearly all the complexes in this class which are presently known contain identical metal centers (M–O–M);[3] a much smaller number having two different metals (M–O–M′) have been prepared.[4] We wish to report the synthesis and unusual chemical properties of organometallic heterodinuclear μ-oxo complexes containing a zirconium and tungsten atom bound to oxygen.

Dinuclear oxaalkyl complexes **3** in Scheme I were obtained in good yield by treatment of the appropriate carbon-bound tungsten enolates[5] **1** with hydridozirconium complex **2** under rigorously air- and moisture-free conditions.[6-8] Complex **3d** exists as two diastereomers which are separable by recrystallization. Spectral data showed no evidence for W–Zr interaction in any of these

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(1) (a) Sykes, A. G.; Weil, J. A. *Prog. Inorg. Chem.* **1970**, *13*, 1. (b) Jezovska-Trzebiatowska, B. *Coord. Chem. Rev.* **1968**, *3*, 255. (c) Evans, W. J.; Grate, J. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 405 and references therein.

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(3) Some representative examples: (a) M = Ti, Zr, Hf: Wailes, P. C.; Coutts, R. S. P.; Weigold, H. *Organometallic Chemistry of Titanium, Zirconium, and Hafnium*; Academic Press: New York, 1974; pp 45–45, 126–130. (b) M = Zr, Hf: Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472. (c) M = Ta: Cotton, F. A.; Najjar, R. G. *Inorg. Chem.* **1981**, *20*, 1866. (d) M = Cr: Liston, D. J.; West, B. O. *Inorg. Chem.* **1985**, *24*, 1568. M = Mo: Spence, J. T. *Coord. Chem. Rev.* **1983**, *48*, 59. (e) Mo, W polyoxo anions: Day, V. W.; Klemperer, W. G. *Science (Washington, D.C.)* **1985**, *228*, 533. (f) M = W: Feistein-Jaffe, I.; Gibson, D.; Lippard, S. J.; Schrock, R. R.; Spool, A. *J. Am. Chem. Soc.* **1984**, *106*, 6305. (g) M = Re: Herrmann, W. A.; Serrano, R.; Schefer, A.; Kusthardt, U. *J. Organomet. Chem.* **1984**, *272*, 55. (h) M = Fe: Murray, K. S. *Coord. Chem. Rev.* **1974**, *12*, 1. (i) M = Fe: Armstrong, W. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4837. (j) M = Ru: Collman, J. P.; Barnes, C. E.; Brothers, P. J.; Collins, T. J.; Ozawa, T.; Gullucci, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 5151. (k) M = Os: Chakrawarty, A. R.; Cotton, F. A.; Schwotzer, W. *Inorg. Chem.* **1984**, *23*, 99. (l) M = Ir: Brownlee, G. S.; Carty, P.; Cash, D. H.; Walker, A. *Inorg. Chem.* **1975**, *14*, 323. (m) M = U: Reynolds, J. E.; Zalkin, A.; Templeton, D. H.; Edelstein, N. M. *Inorg. Chem.* **1977**, *16*, 1090. (n) M = Sm: see ref 1c.

(4) (a) Audett, J. D.; Collins, T. J.; Santarsiero, B. D.; Spies, G. H. *J. Am. Chem. Soc.* **1982**, *104*, 7352. (b) Shapley, J. R.; Park, J. T.; Churchill, M. R.; Ziller, J. W.; Beanan, L. R. *J. Am. Chem. Soc.* **1984**, *106*, 1144. (c) Saxton, R. J.; Olson, L. W.; Wilson, L. J. *J. Chem. Soc., Chem. Commun.* **1982**, 984. (d) Carriedo, G. A.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1597. (e) Liston, D. J.; Kennedy, B. J.; Murray, K. S.; West, B. O. *Inorg. Chem.* **1985**, *24*, 1561. (f) Che, T. M.; Day, V. W.; Francesconi, L. C.; Fredrich, M. T.; Klemperer, W. G. *Inorg. Chem.* **1985**, *24*, 4055 and references therein.

(5) (a) Ariyaratne, J. K. P.; Bierrum, A. M.; Green, M. L. H.; Ishaq, M.; Prout, C. K.; Swainwick, M. G. *J. Chem. Soc. A* **1969**, 1309. (b) Hillis, J.; Ishaq, B.; Gorewit, B.; Tsutsui, J. *J. Organomet. Chem.* **1976**, *116*, 91. (c) Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1985**, *107*, 3724 and work in progress.

(6) This strategy has been employed in the synthesis of other types of polynuclear complexes. See, for example: (a) Afzal, D.; Lenhert, P. G.; Lukehart, C. M. *J. Am. Chem. Soc.* **1985**, *107*, 2023. (b) Jacobsen, E. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2023. (c) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218.

(7) No attack of hydride on the carbonyl groups attached to tungsten was observed.

(8) Full experimental, spectroscopic, and analytical data are provided in the supplementary material.

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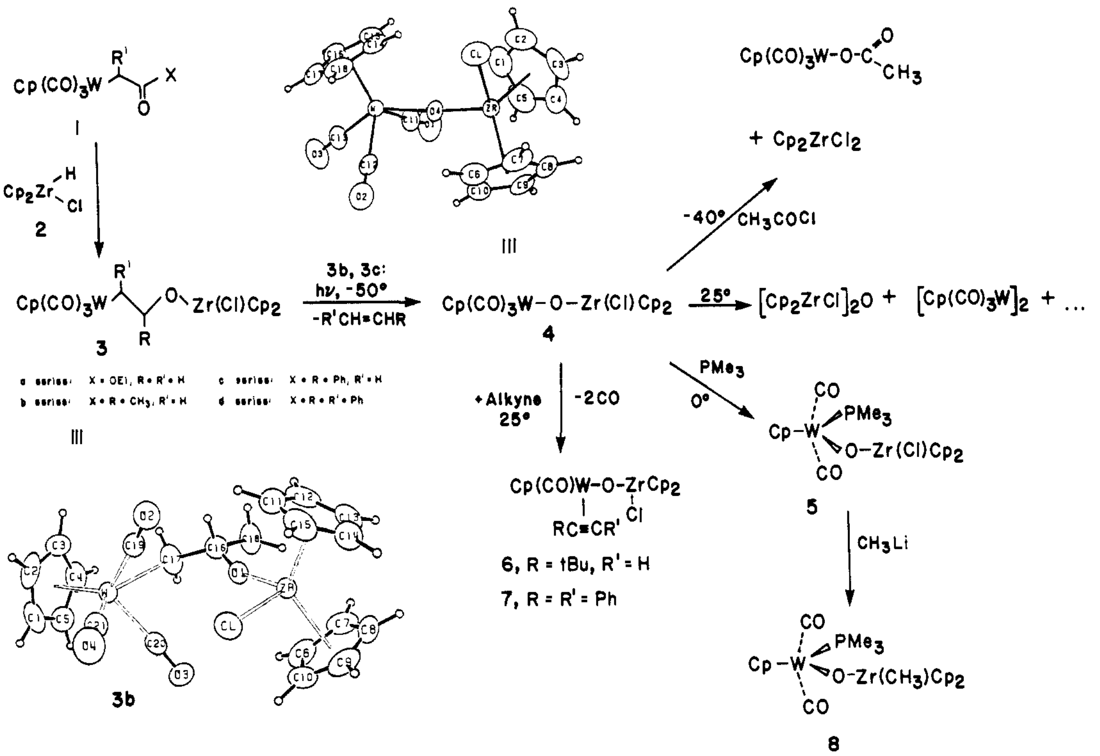
Scheme I



materials. The structure of **3b**, determined by X-ray diffraction,[9] confirmed this deduction and revealed the extended-chain structure shown in the ORTEP diagram included in Scheme I.

All the complexes **3** illustrated in Scheme I undergo decomposition with extrusion of the two-carbon fragment as alkene. The conditions necessary for this decomposition and the organometallic products formed depend upon the substituents R and R'. Parent complex **3a** and monophenyl complex **3c** lead slowly at 45 °C to ethylene and stilbene and a complex mixture of organometallic products [$[Cp(CO)_3W]_2$[10] (56–66%); $Cp_2(Cl)Zr–O–Zr(Cl)Cp_2$[11] (75–85%); $[Cp_2ZrO]_3$[12] (5–10%); $Cp(CO)_3W–Cl$[13] (20–24%)]. Decomposition of the two diastereomers of **3d** is somewhat cleaner, giving *trans*-stilbene and mostly $[Cp_2Zr(Cl)]_2O$ and $[CpW(CO)_3]_2$.[14] An intermediate can be detected by NMR in the decomposition of the more rapidly reacting (threo) isomer. This intermediate, subsequently (see below) identified as bridging oxo complex **4**, can be generated cleanly (70% NMR yield) by irradiation of **3b** or **3c** at −50 °C. The material is thermally sensitive, and isolation in pure form (36% yield) has only been possible with considerable loss of material. Decomposition of **4** in benzene or other nonprotic solvents produces a mixture containing $[Cp_2Zr(Cl)]_2O$ (100%) and $[CpW(CO)_3]_2$ similar to that observed in the thermal decomposition of **3d**.

The heteronuclear μ-oxo dimer was characterized by spectroscopic and combustion analysis, and its structure was confirmed by X-ray diffraction (Scheme I).[15] The Zr–O–W linkage is almost exactly linear (175.7°) but very asymmetric due to a longer W–O bond ($r_{W-O} = 2.065$ Å; $r_{Zr-O} = 1.871$ Å). The IR spectrum contains a broad strong absorbance at 789 cm^{-1} which shifts to 750 cm^{-1} upon ^{18}O substitution at the μ-oxo position. These values are typical of reported asymmetric stretching vibrations of M–O–M and M–O–M' complexes.[1b,16] The electronic spectrum contains a single broad band in the visible region with $\lambda_{max} = 466$ nm [$\epsilon = 892$ L/(mol cm)]. The ^{17}O NMR spectrum of an enriched sample shows a single resonance at δ 194 (vs. H_2O capillary insert). Chemical shifts of ^{17}O nuclei in both organic and inorganic molecules have been correlated with the π-bond order at oxygen.[17] Bridging oxides containing metals in their highest oxidation state have reported shifts of 360–900 ppm; shifts for $[Cp'_2Zr(X)]_2O$ ($Cp' = C_5H_5$, C_5Me_5) complexes fall in the range 526–581 ppm.[18] The relatively high field shift of the asymmetric μ-oxo complex **4** is consistent with significantly reduced π-bonding between the oxygen and one of the metals (presumably tungsten), compared with that observed in high-valent homodinuclear analogues.

The chemical reactivity of **4** depends dramatically on the nature of the substrate employed. The electrophilic reagent acetyl chloride, for example, reacts with **4** within 5 min at −40 °C. Surprisingly, this transformation results in cleavage of the (presumably) stronger Zr–O bond of the bridge, giving Cp_2ZrCl_2 (100%) and the previously unreported acetate complex $Cp(CO)_3W(OCOCH_3)$ (82%).[19] By comparison, the homodinuclear complex $[Cp_2Zr(Cl)]_2O$ reacts slowly with acetyl chloride at room temperature, eventually affording Cp_2ZrCl_2 as the only organometallic product.[20]

Despite the fragility of the metal–oxygen bonds implied by the

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[9] Both crystal structures described in this paper were determined by Dr. F. J. Hollander of the UC Berkeley College of Chemistry X-ray Diffraction Facility (CHEXRAY). Data for **3b**: monoclinic crystals; space group $P2_1/n$, with $a = 11.7495$ (15) Å, $b = 14.2756$ (17) Å, $c = 12.4871$ (17) Å, $\beta = 91.956$ (11)°, and $V = 2093.3$ (8) Å^3; 2732 reflections; final $R = 2.26\%$. Details of the structure determination are provided as supplementary information.

[10] (a) Wilkinson, G. *J. Am. Chem. Soc.* **1954**, *76*, 209. (b) Birdwhistell, R.; Hackett, P.; Manning, A. R. *J. Organomet. Chem.* **1978**, *157*, 239.

[11] Reid, A. F.; Shannon, J. S.; Swan, M. M.; Wailes, P. C. *Aust. J. Chem.* **1965**, *18*, 173.

[12] Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1979**, *101*, 1767.

[13] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104. Hoffman, N. W. *Inorg. Chim. Acta* **1984**, *88*, 59.

[14] We have not been able to determine the fate of the second oxygen atom; no CO_2 is detected in the product mixture. This problem is currently under study.

[15] X-ray data for **4**: monoclinic crystals; space group $P2_1/n$, with $a = 11.1729$ (9) Å, $b = 12.5026$ (10) Å, $c = 13.7658$ (13) Å, $\beta = 100.924$ (8)°, and $V = 1888.1$ (5) Å^3; 2458 reflections; final $R = 3.22\%$. Details of the structure determination are provided as supplementary information.

[16] San Filippo, J., Jr.; Grayson, R. L.; Sniadoch, H. J. *Inorg. Chem.* **1976**, *15*, 269 and references therein.

[17] (a) Klemperer, W. G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 246 and references therein. (b) Miller, K. F.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 984.

[18] Reference 3b; Jacobsen, Jacobsen, E. N.; Bergman, R. G., unpublished results.

[19] No reaction was observed between $Cp_2(Cl)Zr(OCOCH_3)$ and $Cp(CO)_3W–Cl$ under these conditions.

[20] The acetate complex $Cp_2(Cl)Zr(O_2CCH_3)$ can be detected by ^1H NMR spectroscopy during the course of the reaction.

thermal decomposition of **4** and its reaction with acetyl chloride, reaction with nucleophiles leaves these bonds intact. Thus, treatment of the μ-oxo complex with excess PMe$_3$ at 0 °C in CH$_2$Cl$_2$ or toluene leads stereospecifically[21] to cis-substitution product **5** (Scheme I) in 95% NMR and 71% isolated yield. Reaction of **4** with *tert*-butyl- or diphenylacetylene leads to the (μ-oxo)(π-alkyne) complexes **6** (68% yield by NMR; 61% isolated) and **7** (75% by NMR; 71% isolated),[8] to our knowledge the first example of this class of molecules.[22] Reaction of **5** with methyllithium also does not cleave the M–O–M′ linkage. Substitution in this case takes place at zirconium and leads to methylzirconium complex **8** in 55% yield. Reaction of methyllithium with the homonuclear dimer Cp$_2$(Cl)Zr–O–Zr(Cl)Cp$_2$ also leads to Zr–Cl bond cleavage, giving Cp$_2$(CH$_3$)Zr–O–Zr(CH$_3$)Cp$_2$.

Mechanistic studies now under way are aimed at improving our understanding of the unusual selectivities of these transformations.

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Supplementary Material Available: Experimental procedures for the preparation of complexes **1d**, **3–8**, and Cp(CO)$_3$W(O$_2$CCH$_3$) including spectroscopic and analytical data; reference to the preparation of enolates **1a–c**; experimental details of the X-ray diffraction studies of complexes **3b** and **4**, including crystal and data collection parameters, tables of positional parameters, general temperature factors, intramolecular distances and angles (25 pages); structure factor tables for **3b** and **4** (30 pages). Ordering information is given on any current masthead page.

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[21] These CO-substitution reactions occur more rapidly than those in Cp(CO)$_3$W-R (R = alkyl) complexes. This may be a cis-labilization effect; cf.: (a) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3160. (b) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 398.

[22] Shapley and co-workers have synthesized a trinuclear μ_2-oxo complex containing a (μ_3-η^2-C$_2$H$_2$) ligand.[4b]

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cis-[Bis(dicyclohexylphosphino)ethane]platinum(0) Reacts with Unactivated Carbon-Hydrogen Bonds[1]

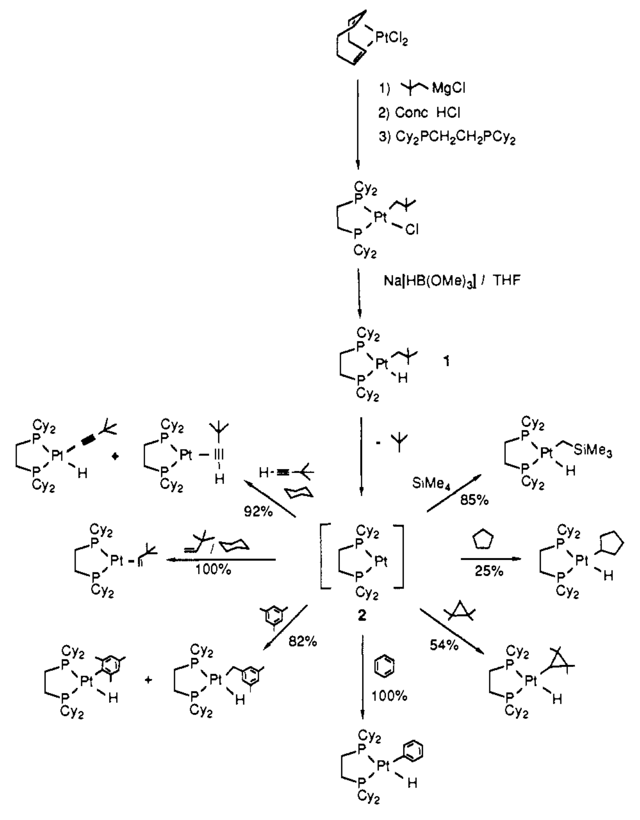
Marifaith Hackett,[2] James A. Ibers,[3] Peter Jernakoff,[2] and George M. Whitesides*[2]

Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received July 15, 1986

Although platinum(0) is centrally important in heterogeneous catalytic reforming of petroleum,[4] the only soluble platinum complexes that react with saturated hydrocarbons are platinum chlorides and acetates.[5] In particular, and by contrast with iridium, rhodium, and the other transition metals that have provided the basis for the recent major advances in carbon–hydrogen bond activation,[5,6] no phosphine-stabilized platinum species has been reported that reacts *inter*molecularly with unactivated C–H bonds, although *intra*molecular reaction is facile.[7] Here, we report that thermal reductive elimination of neopentane from *cis*-hydrido-

Scheme I[a]



[a] All reactions were conducted at 69 °C, except for the thermolyses in cyclopentane and tetramethylcyclopropane, which were run at 45 °C. Yields were determined by ^{31}P NMR spectroscopy and refer to the combined yield if two products were obtained. Cy = cyclohexyl.

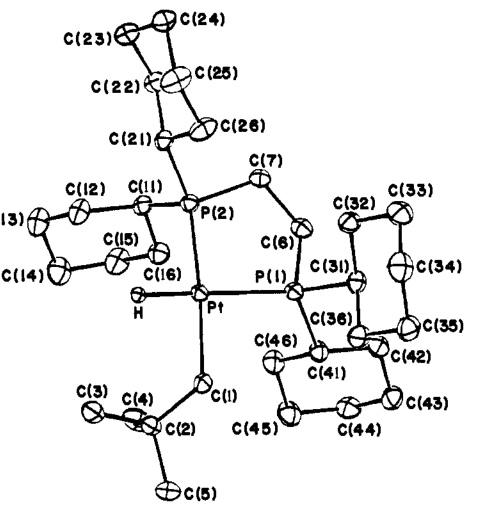


Figure 1. Drawing of PtH(CH$_2$CMe$_3$)(Cy$_2$PCH$_2$CH$_2$PCy$_2$). Ellipsoids are drawn at the 50% probability level. Except for the hydride ligand, H atoms are omitted for the sake of clarity. Selected bond distances and angles: Pt–H, 1.56 (5); Pt–C (1), 2.125 (5); Pt–P(1), 2.278 (2); Pt–P(2), 2.253 (2) Å; H–Pt–C(1), 82 (2)°; C(1)–Pt–P(1), 95.3 (1)°; P(1)–Pt–P(2), 88.16 (6)°; P(2)–Pt–H, 96 (2)°.

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[1] Supported by the National Science Foundation, Grants CHE 85-08702 (to G.M.W.), CHE 83-08078 (to Prof. N. J. Cooper for P.J.), and CHE 83-08076 (to J.A.I.).

[2] Harvard University.

[3] Northwestern University.

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[7] See, for example: Cheney, A. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans* **1972**, 754–763. Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713–6725. McCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 3396–3403, 3404–3410.

0002-7863/86/1508-8094$01.50/0