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_2Cl_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.

Acknowledgment. We are grateful for financial support of this work from the National Science Foundation through Grant 8420979. Fellowship support was provided by the Regents of the University of California (to E.N.J.) and the National Science Foundation (to M.K.T.). We are grateful to Jeffrey J. Doney and Profs. John E. Bercaw and Robert H. Grubbs for helpful discussions and disclosure of results prior to publication.

Supplementary Material Available: Experimental procedures for the preparation of complexes **1d**, **3–8**, and $Cp(CO)_3W(O_2CCH_3)$ 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.

---

[21] These CO-substitution reactions occur more rapidly than those in $Cp(CO)_3W{-}R$ (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_2H_2) ligand.[4b]

---

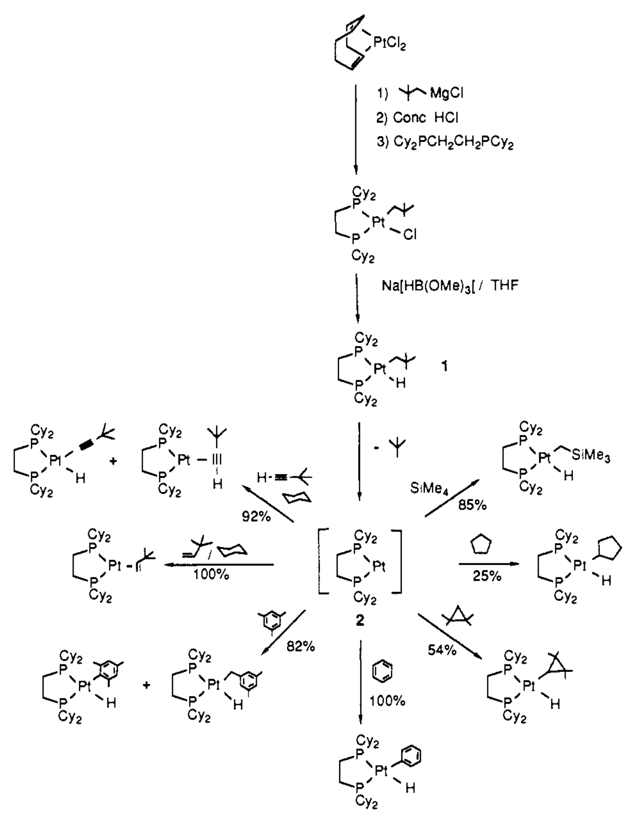
cis-[Bis(dicyclohexylphosphino)ethane]platinum(0) Reacts with Unactivated Carbon-Hydrogen Bonds[1]

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

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.

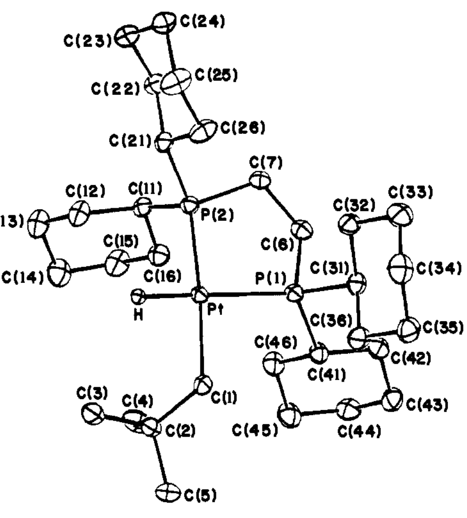


Figure 1. Drawing of $PtH(CH_2CMe_3)(Cy_2PCH_2CH_2PCy_2)$. Ellipsoids are drawn at the 50% probability level. Except for the hydride ligand, H atoms are omitted for the sake of clarity. Selected bond distances and angles: Pt–H, 1.56 (5); Pt–C (1), 2.125 (5); Pt–P(1), 2.278 (2); Pt–P(2), 2.253 (2) Å; 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)°.

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-

---

[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.

[4] Ciapetta, E. G.; Wallace, D. N. *Catal. Rev.* **1971**, *5*, 67–158.

[5] Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Hingham, MA, 1984. Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147–188. Shilov, A. E. *Pure Appl. Chem.* **1978**, *50*, 725–733. Kushch, L. A.; Lavrushko, V. V.; Misharin, Yu. S.; Moravsky, A. P.; Shilov, A. E. *Nouv. J. Chim.* **1983**, *7*, 729–733.

[6] For leading references, see: Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537–1550. Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985**, *107*, 620–631. Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245–269.

[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

neopentyl[bis(dicyclohexylphosphino)ethane]platinum(II) (**1**) produces the reactive intermediate [bis(dicyclohexylphosphino)ethane]platinum(0) (**2**) and that **2** reacts with C–H bonds in saturated and unsaturated hydrocarbons.[8]

Compound **1** was prepared as described in Scheme I.[9] It is unreactive toward water and dioxygen and thermally stable as a crystalline solid. Its structure was established unequivocally by X-ray diffraction (Figure 1).[10] Relevant features of the structure are the cis arrangement of the hydride and alkyl groups and the disposition of the cyclohexyl rings. These rings occupy positions that should minimize intramolecular interactions of their C–H bonds with the platinum center if the solid-state structure persists in solution. We believe that **2** probably has a similarly exposed, unencumbered platinum atom and that the high intermolecular reactivity of **2** reflects, in part, low *intra*molecular reactivity.

Reductive elimination of neopentane from **1** occurs at convenient rates in a variety of solvents at temperatures between 45 and 80 °C (Scheme I); **2**, the inferred intermediate, reacts with C–H bonds in saturated and unsaturated hydrocarbons.[11] Given that very few transition-metal complexes react with saturated hydrocarbons, perhaps the most interesting reactions are those with cyclopentane and 1,1,2,2-tetramethylcyclopropane. Thermolysis of **1** in *n*-hexane or cyclohexane does not yield adducts but instead generates insoluble precipitates.

The decomposition of **1** in benzene is cleanly first order in **1**, with rate constant $k_1 = (2.8 \pm 0.1) \times 10^{-4}\ \mathrm{s}^{-1}$ at 69 °C (determined with the use of ^{31}P NMR spectroscopy). Arrhenius parameters derived from thermolyses at temperatures from 49 to 81 °C are $E_a = 28.0 \pm 0.4$ kcal/mol and $\log A = 14.3 \pm 0.2$. Addition of free bis(dicyclohexylphosphino)ethane has no effect on the rate, but a new product, bis[bis(dicyclohexylphosphino)ethane]platinum(0), forms in competition with **2**. The isotope effect for the reductive elimination of neopentane-d_1 from $L_2Pt(Np)(D)$, $k_H/k_D = 1.5$, is consistent with rate-determining reductive elimination of neopentane,[12] as is the fact that the rate of decomposition is indistinguishable in C_6H_6 and C_6D_6. Increase of the concentration of benzene in mixed benzene/cyclohexane solutions caused a *decrease* in the rate of decomposition and established that benzene was *not* coordinated to **1** before or at the transition state.

We suggest that **2** is a homogeneous model for an "edge" atom in a heterogeneous platinum catalyst. These sites have been shown to be reactive in C–H bond activation in studies with platinum single crystals;[13] **2** is also isolobal[14] with methylene; $:CH_2$.

Acknowledgment. We thank Professor Roald Hoffmann for encouraging and enlightening discussions.

Supplementary Material Available: Spectral and analytical data for the complexes shown in Scheme I and a table of atomic coordinates and thermal parameters (5 pages). Ordering information is given on any current masthead page.

---

(8) Literature precedent suggested that reductive elimination of an alkane from a *cis*-hydridoalkylbis(phosphine)platinum(II) complex would be facile and that the *bent* (bisphosphine)platinum(0) species generated by reductive elimination of neopentane from **1** would be highly reactive. See: Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915–2916. Yoshida, T.; Yamagata, T.; Tulip, T. H.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063–2073. Electron-withdrawing groups on the alkyl ligand stabilize the complex with respect to reductive elimination: Michelin, R. A.; Faglia, S.; Uguagliati, P. *Inorg. Chem.* **1983**, *22*, 1831–1834.

(9) Spectral and analytical data for **1**: ^{1}H NMR (C_6D_6) δ 2.52 ("t" with Pt satellites, $J_{P\text{-}H} = 7$, $J_{Pt\text{-}H} = 78$ Hz, 2 H), 2.25–1.95 (m, 6 H), 1.95–1.0 (m, 51 H), –0.15 (d of d with Pt satellites, $J_{P\text{-}H} = 18$, $J_{P'\text{-}H} = 194$, $J_{Pt\text{-}H} = 1175$ Hz, 1 H); ^{31}P NMR (C_6D_6) δ 75.9 (s with Pt satellites, $J_{Pt\text{-}P} = 1664$ Hz), 62.9 (s with Pt satellites, $J_{Pt\text{-}P} = 1798$ Hz); IR (neat) 2010 cm^{-1}; mp (capillary sealed under Ar) 120–130 °C dec. Anal. Calcd for $C_{31}H_{60}P_2Pt$: C, 53.97; H, 8.77; P, 8.98. Found: C, 54.11; 53.94; H, 8.69, 8.74; P, 8.92, 8.96.

(10) Crystal structure information: $C_{31}H_{60}P_2Pt$, FW = 689.86. Monoclinic, space group $C_{2h}{}^5$-$P2_1/n$. At –150 °C, $a = 11.517$ (8) Å, $b = 15.730$ (11) Å, $c = 17.364$ (13) Å, $\beta = 90.32$ (3)°, $V = 3146$ Å^3 with 4 formula units per cell; $D_{\text{calcd}} = 1.456$ g cm^{-3} (–150 °C); $D_{\text{obsd}} = 1.36$ g cm^{-3} (20 °C); $\mu = 46.22$ cm^{-1}. Data were collected on a CAD4 diffractometer at –150 °C (Mo Kα radiation out to $\theta = 31°$). A total of 10182 unique $F_o{}^2$ values were used in the final refinement of 311 variables. Included in the final model were anisotropic motion of the non-hydrogen atoms and isotropic motion of the hydride ligand. Other H atoms were located on an earlier Fourier map and their positions were idealized in the final refinement. This refinement converged to a value of 0.069 for $R(F^2)$ and for the 7056 F^2 values having $F_o{}^2 > 3\ (F_o{}^2)$ to a value of $R(F)$ of 0.044.

(11) Except for *cis*-hydridoneopentyl[bis(dicyclohexylphosphino)ethane]platinum(II) and (3,3-dimethyl-1-butene)[bis(dicyclohexyl)phosphino)ethane]platinum(0), the platinum-containing reaction products were identified by comparison with independently synthesized, fully characterized complexes. In all cases, the reaction products were indistinguishable by ^{1}H and ^{31}P NMR spectroscopy from the independently synthesized complexes. *cis*-Hydridophenyl[bis(dicyclohexylphosphino)ethane]platinum(II) and (3,3-dimethyl-1-butene)[bis(dicyclohexylphosphino)ethane]platinum(0) were isolated from preparative-scale thermolyses of **1** in benzene and in a cyclohexane solution of 3,3-dimethyl-1-butene, respectively. Spectral and analytical data for all of the complexes shown in Scheme I are available as supplementary material; complete details of the syntheses will be published later. The sole organic product was neopentane, identified by its GC retention time and GC/MS.

(12) Saunders, W. H., Jr. In *Techniques of Chemistry*, 3rd ed.; Lewis, E. S., Ed.; Wiley: New York, 1974; Vol. 6, Chapter 5. Melander, L.; Saunders, W. H., Jr. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980.

(13) Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell University Press: Ithaca, NY, 1981; Chapter 9.

(14) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711–724. Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006–2026.

Reaction of Group 4 Metal η^2-Acyls with Pyridine: Formation of α,α-Disubstituted-2,6-pyridinedimethoxide Ligands

Phillip E. Fanwick, Lisa M. Kobriger, Anne K. McMullen, and Ian P. Rothwell*[1]

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received July 28, 1986

Over the last 10 years the early-transition-metal, lanthanide, and actinide η^2-acyl functional group has received considerable study by both synthetic and theoretical chemists.[2–4] This has been prompted by the unique reactivity of these groups compared to their more well-studied, later-transition-metal analogues. We wish to report here the observed insertion of group 4 metal η^2-acyls into the ortho-CH bonds of pyridine ligands. This result not only demonstrates a novel reactivity for the functionality but also represents a high-yield synthetic route to α,α-disubstituted-2,6-pyridinedimethoxide ligands; ligands that have received recent attention by a number of research groups.[5]

Hydrocarbon solution of the compounds $M(OAr')_2(CH_3)_2$ (M = Zr, Hf; OAr′ = 2,6-di-*tert*-butylphenoxide)[7b] react with carbon

---

(1) (a) Camille and Henry Dreyfus Teacher-Scholar, 1985–1990. (b) Fellow of the Alfred P. Sloan Foundation, 1986–1988.

(2) (a) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (b) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. (c) Fachinetti, G.; Fochi, G.; Floriani, C.; Stoeckli-Evans, H. *J. Chem. Soc., Dalton Trans.* **1977**, 2297. (e) Curtis, M. D.; Shiu, K. B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550 and references therein. (f) Marsella, J.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596. (g) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 218. (h) Gell, K. I.; Posin, G.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846.

(3) (a) Evans, W. J. *Adv. Organomet. Chem.* **1985**, *24*, 131. (b) Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 706. (c) Marks, T. J.; Day, V. W. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragala, I. L., Eds.; Dordrecht: Holland, 1986. (d) Moloy, K. G.; Fagan, P. J.; Manriquez, J. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 56. (e) Marks, T. J. *Science (Washington, D.C.)* **1982**, *217*, 989. (f) Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051. (g) Maata, E. A.; Marks, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 3576.

(4) (a) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440. Tatsumi, K.; Nakamura, A.; Hoffmann, R., *Organometallics* **1985**, *4*, 404.

(5) (a) Hawkins, J. M.; Dewan, J. C.; Sharpless, K. B., *Inorg. Chem.* **1986**, *25*, 1501. (b) Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 1768.

(6) Anal. Calcd for $ZrO_4N_2C_{42}H_{58}$ (**1**): C, 67.61; H, 7.84; N, 3.75. Found: C, 67.62; H, 8.21; N, 3.75%. $HfO_4N_2C_{42}H_{58}$ (**2**): C, 60.53; H, 7.01; N, 3.36. Found: C, 60.10; H, 7.18; N, 2.95%.

0002-7863/86/1508-8095$01.50/0