The reverse reaction can be demonstrated with **16** using a large excess of acetonitrile to give, after 2 days at ambient temperature, $CpRu(CH_3CN)_3^+$, clearly indicative of the slow nature of this displacement reaction (eq 3).[13]

$$16 + \text{excess } CH_3CN \rightarrow CpRu(CH_3CN)_3^+ + 6 \quad (3)$$

The overall results demonstrate that steric effects and nitrogen nonbonding electron availability appear to be contributing factors in the formation of both N- and π-bonded complexes of $CpRu^+$.[2] The mechanism of these N to π rearrangements could possibly occur via N(η^1) to η^2 then to η^4 intermediates (ring slippage), which would allow a stepwise process to the π-bonded (η^6) product with loss of the acetonitrile ligands (η^2–η^4–η^6).[9,13,14]

The dramatic differences between our pyridine bonding results and Chaudret and Jalon's[4] may be a consequence of possible steric and electronic differences between Cp and Cp*. For example, Cp* places higher electron density on Ru than Cp and this may preclude N-bonding, while strongly favoring π-bonding (arenophilicity) at Cp^*Ru^{2+} as is observed.[4,13]

We are continuing our studies on the bonding and catalytic activity of rhodium and ruthenium cationic complexes with nitrogen heterocyclic compounds and the mechanistic aspects of the N–π rearrangement.

Acknowledgment. The studies at LBL were supported by the Director, Office of Energy Research, Office of Basic Energy Science, Chemical Sciences Division of the U. S. Department of Energy, under Contract No. DE-AC03-76SF00098.

(13) McNair, A. M.; Mann, K. R. *Inorg. Chem.* **1986**, *25*, 2519.
(14) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 7555 and references therein.

Pentakis(trimethylphosphine)osmium(0)

Susan P. Ermer, Ronald S. Shinomoto, Mark A. Deming, and Thomas C. Flood*

Department of Chemistry, University of Southern California Los Angeles, California 90089-0744

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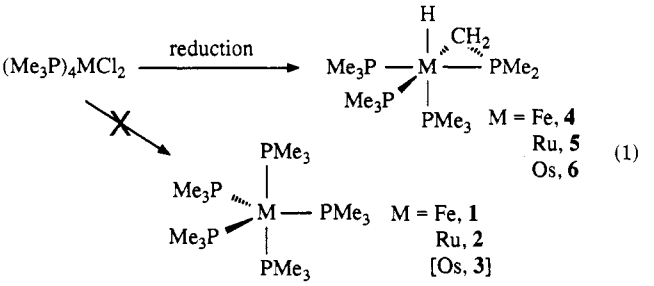
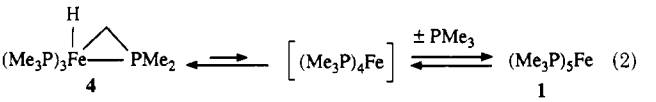
Summary: The new complex $(Me_3P)_5Os$ (**3**) has been prepared and characterized. It is nonrigid at ambient temperature on the NMR time scale. Treatment of **3** with triflic acid yielded $[(Me_3P)_5OsH]OTf$ (**7**). Thermolysis of **3** above 40 °C in neat THF, benzene, neohexene, tetramethylsilane, or alkane solvent results in quantitative formation of $(Me_3P)_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ (**6**). At constant $[PMe_3]$ the conversion of **3** to **6** is cleanly first order, and the rate is strongly inhibited by the added PMe_3. In the presence of a large excess of $P(CD_3)_3$, the rate of ligand exchange with **3** can be measured; preliminary data yield an E_a of ca. 28 kcal/mol for PMe_3 dissociation.

Pentakis(trimethylphosphine) complexes of zerovalent iron (**1**), ruthenium (**2**), and osmium (**3**) have not been previously known, although species such as L_5M^0 (M = Fe, Ru, Os; L = PF_3, $P(OCH_3)_3$) and combinations of these with PMe_3 have been prepared.[1] All attempts to prepare $(Me_3P)_5M$ have instead yielded cyclometalated complexes as shown in eq 1. A number of years ago, Karsch and



(1)

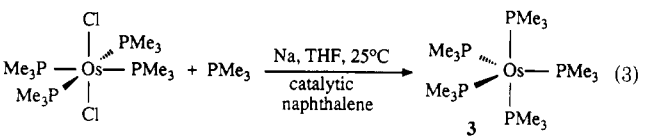
Schmidbaur[2] and Muetterties[3] prepared iron complex **4**. They found evidence for a facile, reversible reductive elimination and complexation by L (PMe_3) to form **1** in concentrations not directly detectable by NMR (eq 2).



(2)

Much of the reactivity of **4** was rationalized as arising from a small equilibrium concentration of L_4Fe. More recently, Werner and co-workers have prepared **5** and **6** and have investigated their chemistry.[4]

We have recently employed the Werner complex **6** to gain access to a set of complexes *cis*-$L_4Os(H)R$.[5] In an attempt to enhance an already good yield, the preparation of **6** was carried out in the presence of a 10-fold excess of L (eq 3). Instead of the characteristic spectrum of **6**,



(3)

$^{31}P\{^1H\}$ NMR (THF) revealed a singlet at δ −56.3 and just traces of resonances for **6**. The $^{13}C\{^1H\}$ NMR spectrum contained a broad resonance at δ 30.8 and the ^1H NMR a broad singlet at δ 1.5. At −100 °C the ^{31}P singlet split into a quartet at δ −45.4 (J = 35 Hz) and a triplet at −61.8 ppm. ^1H resonances were obscured by THF, and the ^{13}C resonance split into two broad, featureless peaks at δ 27 and 32 ppm. These spectral characteristics are most consistent with L_5Os (**3**) with a nonrigid, trigonal-bipyramidal structure.

Complex **3** is stable at ambient temperature in the sealed tube in which it is prepared, but it is very sensitive to

(1) Some examples of homoleptic compounds: $Fe[P(OCH_3)_3]_5$: Muetterties, E. L.; Rathke, J. W. *J. Chem. Soc., Chem. Commun.* **1974**, 850–851. $Ru[P(OCH_3)_3]_5$: Jesson, J. P.; Cushing, M. A.; Ittel, S. D. *Inorg. Synth.* **1980**, *20*, 80–81. $Os[P(OCH_3)_3]_5$: English, A. D.; Ittel, S. D.; Tolman, C. A.; Meakin, P.; Jesson, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 117–120. $Ru(PF_3)_5$ and $Os(PF_3)_5$: Kruck, V. T.; Prasch, A. *Z. Anorg. Allg. Chem.* **1969**, *371*, 1–22.
(2) (a) Karsch, H. H.; Klein, H.-F.; Schmidbaur, H. *Chem. Ber.* **1977**, *110*, 2200–2212. (b) Karsch, H. H.; Klein, H.-F.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 637–638.
(3) (a) Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272–3273. (b) Harris, T. V.; Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 6966–6977.
(4) (a) Werner, H.; Werner, R. *J. Organomet. Chem.* **1981**, *209*, C60–C64. (b) Werner, H.; Gotzig, J. *Organometallics* **1983**, *2*, 547–549. (c) Gotzig, J.; Werner, R.; Werner, H. *J. Organomet. Chem.* **1985**, *285*, 99–114.
(5) (a) Desrosiers, P. J.; Shinomoto, R. S.; Flood, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 1346–1347. (b) *Ibid.*, **1986**, *108*, 7964–7970. (c) Harper, T. G. P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7915–7916. (d) Desrosiers, P. J.; Harper, T. G. P.; Shinomoto, R. S.; Flood, T. C., submitted for publication.

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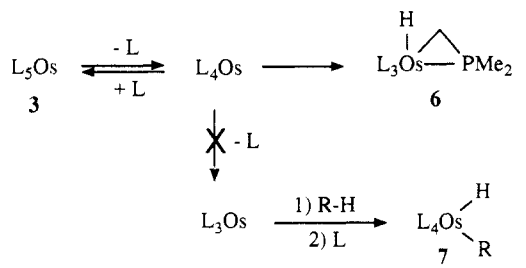
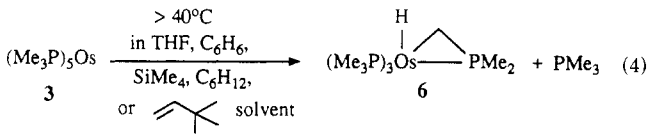
Scheme I



manipulation. Filtration of its solutions, even through carefully dried fritted disks results in formation of L_5OsH^+, identifiable by its characteristic ^{31}P NMR and its ^1H NMR hydride resonance (see below). We assume that the counterion is probably hydroxide, but we have not characterized this form of the salt. Centrifugation and decantation of solutions of **3** followed by careful solvent removal under vacuum yields solid ranging in color from off-white to orange, depending on the sample. Redissolution in various solvents often yields solutions of **3** which ^{31}P NMR shows to be clean and largely free of L. However, unless solvents and apparatus are scrupulously dried, substantial quantities of L_5OsH^+ are formed, even to the point of its being the only material present. Careful concentration of a pentane solution of **3** and cooling at −20 °C yielded a large, flat, nearly colorless crystal of **3** which displayed clean NMR spectra upon redissolution.[6]

Treatment of a THF solution of **3** at −78 °C with an ether solution of triflic acid yielded $[L_5OsH]OTf$, which has been fully characterized.[7] Thermolysis of **3** above 40 °C in neat THF, benzene, neohexene, tetramethylsilane, or alkane solvent results in quantitative formation of the Werner complex **6** (eq 4); no trace of product arising from



attack on the solvent can be detected even in benzene or neohexene. (We know, for example, that $L_3Os(H)$(neopentyl) activates benzene,[5a,b] and L_3Os activates saturated C-H bonds intermolecularly.[5c,d]) In the presence of sufficient free L to keep [L] essentially constant, the conversion of **3** to **6** is cleanly first order, and the rate is strongly inhibited by the added L.

In the presence of a large excess of $P(CD_3)_3$, L′, the rate of ligand exchange with **3**, can be measured.[8] Preliminary rate data over the range of 30–50 °C yield an E_a of ca. 28 kcal/mol[8] for L dissociation. This rapid ligand exchange and the inhibition of reaction 4 by added L demonstrate that reaction 4 proceeds via presumably square-planar, phosphine-dissociated intermediate L_4Os, as in Scheme I. Intermediate L_4Os does not undergo dissociation of a second L to form L_3Os because we know that L_3Os would react with C_6H_6, $SiMe_4$, or neohexene with C–H activation to afford molecules of type **7**, none of which is observed.[5d]

Other reactions of **3** are under investigation.

Acknowledgment. We thank the National Science Foundation (CHE-8705228) for support of this work. Loans of heavy metal salts by Johnson Matthey Co. are gratefully acknowledged.

(6) Elemental Anal. Calcd for $C_{15}H_{45}P_5Os$ (**3**): C, 31.58; H, 7.95. Found: C, 31.01; H, 8.26.

(7) Data for L_5OsH^+OTf: ^1H NMR (THF-d_8) δ −12.22 (dp, 1 H, J_{PH} = 54.3, 21.7 Hz), 1.57 (d, 9 H, J_{PH} = 6.6 Hz), 1.75 (vt, 36 H, J_{PH}(apparent) = 5.3 Hz); $^{31}P\{^1H\}$ NMR (THF) δ −55.8 (d, 4 P, J_{PP} = 18.1 Hz), −60.9 (p, 1 P); $^{31}P\{$selective ^1H, Os*H* coupled$\}$ δ −55.8 (dd, J_{PH} = 18.0 Hz), −60.9 (dp, J_{PH} = 42.4 Hz); in this experiment, the ^1H decoupling band is centered at ca. δ + 5 ppm, and the hydride is slightly decoupled giving smaller hydride J_{PH} in the ^{31}P spectrum than in the ^1H spectrum. Anal. Calcd for $C_{16}H_{46}F_3O_3OsP_5S$: C, 26.63; H, 6.42. Found: C, 26.81; H, 6.56.

(8) The rate of exchange of L_5Os with L′ is monitored by ^1H NMR by following the disappearance of coordinated L at δ 1.5 and appearance of free L at δ 0.8. This rate is the composite of the rate for all five sequential displacements of L by L′ to form $(L')_5Os$. Assuming a negligible isotope effect on each subsequent displacement, k_{obsd} is 5 k_{dissoc}.

Synthesis and Reactivity of Ruthenium Hydride Complexes of Chelating Triphosphines. 2. X-ray Structure Determination of the Novel Compound Ru(CCPh)(η^3-PhC$_3$CHPh)(Cyttp) (Cyttp = $C_6H_5P(CH_2CH_2CH_2P(c\text{-}C_6H_{11})_2)_2$)[1]

Guochen Jia,*,†,2a Arnold L. Rheingold,*,2b and Devon W. Meek‡,2a

Departments of Chemistry, The Ohio State University Columbus, Ohio 43210 and University of Delaware Newark, Delaware 19716

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Summary: The reaction of RuH_4(Cyttp) with phenylacetylene under mild conditions gives a unique type of compound Ru(CCPh)(η^3-PhC$_3$CHPh)(Cyttp) (**1**) which contains an acetylide and the unusual η^3-PhC$_3$CHPh carbon–carbon coupling product as ligands. Phosphorus-31, ^1H, and $^{13}C\{^1H\}$ NMR data in solution are consistent with the results of an X-ray single-crystal structure determination of **1**. This unusual complex contains the chelating triphosphine Cyttp in a meridional arrangement around ruthenium, a linear acetylide, and the η^3-PhC$_3$CHPh ligand, which is probably formed by end-to-end coupling of two phenylacetylene fragments.

During a study of the reactivity of acetylenes with RuH_4(Cyttp),[3] we found that a carbon–carbon bond formation reaction of phenylacetylene occurred under mild conditions. The isolated ruthenium complex Ru(CCPh)(η^3-PhC$_3$CHPh)(Cyttp) contains a linear acetylide and a novel η^3-PhC$_3$CHPh ligand, which might be considered as an intermediate in catalytic oligomerization or polymerization reactions of terminal acetylenes. We report herein the synthesis and structure of this unusual compound.

Treatment of RuH_4(Cyttp) with excess phenylacetylene in benzene at room temperature resulted in formation of Ru(CCPh)(η^3-PhC$_3$CHPh)(Cyttp) (eq 1).[4] The product is a red solid, which was isolated in 86% yield, based on

† Present address: Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1.

‡ Deceased December 7, 1988.

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(2) (a) The Ohio State University. (b) University of Delaware.

(3) Jia, G.; Meek, D. W. *J. Am. Chem. Soc.* **1989**, *111*, 000.

(4) A mixture of 0.3 mL of phenylacetylene and RuH_4(Cyttp) (ca. 0.40 mmol, prepared from the reaction of 0.30 g of $RuCl_2$(Cyttp) with excess NaH) in 30 mL of benzene was stirred at room temperature for 3 h to give a deep red solution. The reaction mixture was then pumped to dryness. The residue was washed with 10 mL of MeOH to give a red powder. The powder was then collected on a filter frit, washed with MeOH, and dried under vacuum overnight; yield 0.34 g, 86% based on $RuCl_2$(Cyttp). X-ray quality crystals were obtained by slowly evaporating solvents from a saturated solution in CH_2Cl_2/MeOH with a stream of argon. Elemental Anal. Calcd: C, 72.63; H, 7.82. Found: C, 72.57; H, 7.83.

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