knowledge **2** is the first example of a mixed diaryltin(II) compound.

Compound **2** readily undergoes oxidative addition reactions. This is reflected, for example, in the instantaneous formation of {2,6-bis[(dimethylamino)methyl]phenyl}-methyl(4-tolyl)tin(IV) iodide (**3**) when MeI is added to a benzene solution of **2**. Since **3** is insoluble in apolar solvents like benzene but very soluble in polar solvents like methanol, it is most likely ionic in nature. An ionic formulation for **3** (see Scheme I) is supported by its ^{1}H NMR data,[15] which are comparable with those of the earlier reported {2,6-bis[(dimethylamino)methyl]phenyl}methylphenyltin(IV) bromide, whose ionic character was unambiguously proved by an X-ray crystal structure determination.[16]

Reaction of **2** with I_2 affords, based on ^{1}H NMR data,[15] hexacoordinate *trans*-{2,6-bis[(dimethylamino)methyl]-phenyl}4-tolyltin(IV) diiodide (**4**). This geometry is in accord with the observation that the two organic groups in hexacoordinated diorganotin dihalide complexes are always mutually trans.[19] In contrast a cis oxidative-addition product is obtained from the reaction of I_2 with {2,6-bis[(dimethylamino)methyl]phenyl}4-tolylplatinum(II), for which it has been proposed on steric grounds that trans oxidative-addition cannot take place.[20] Finally, it is to be noted that in the initial step of the reaction of **2** with I_2 we cannot, as yet, exclude formation of a cis oxidative-addition product, which then rearranges to the trans isomer **4**. This topic is currently under investigation.

Acknowledgment. Thanks are due to Dr. D. M. Grove for critical and stimulating discussions.

Supplementary Material Available: Tables of fractional coordinates of the non-hydrogen atoms, anisotropic thermal parameters, fractional coordinates of the hydrogen atoms, bond distances and angles of the non-hydrogen atoms, and bond distances and angles of the hydrogen atoms (7 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

(19) Harrison, P. G. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 7, Chapter 26.

(20) van Koten, G. Plenary lecture, XIIIth International Conference on Organometallic Chemistry, Torino, Italy, 1988; *Pure Appl. Chem.*, in press.

Bonding Studies of Nitrogen Heterocyclic Ligands to (η^5-Cyclopentadienyl)ruthenium Cation: A Novel Nitrogen to π Rearrangement

Richard H. Fish,* Hoon-Sik Kim, and Raymond H. Fong
Lawrence Berkeley Laboratory, University of California
Berkeley, California 94720

Received January 9, 1989

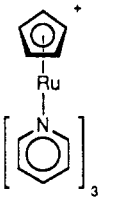
Summary: The nitrogen heterocyclic ligands, pyridine (**1**), 2-methylpyridine (**2**), 2,4-dimethylpyridine (**3**), 2,4,6-trimethylpyridine (**4**), quinoline (**5**), 2-methylquinoline (**6**), and 1,2,3,4-tetrahydroquinoline (**7**), were reacted with (η^5-cyclopentadienyl)ruthenium cation [$CpRu(CH_3CN)_3^+X$, X = PF_6] to determine preferences for nitrogen (N) versus π-bonding. Ligands **1–3** and **5** formed N-bonded complexes, while **4**, **6**, and **7** formed π- (η^6-) bonded complexes. A novel N(η^1) to π(η^6) rearrangement was discovered for the N-bonded $CpRu^+$ complexes of ligands **2**, **3**, and **5**.

The bonding mode of nitrogen heterocyclic ligands to rhodium and ruthenium complexes that have been found to act as homogeneous catalysts has been of considerable interest due to its important role in the regioselective hydrogenation of the nitrogen-containing ring of these model coal compounds.[1] Indeed, we recently reported on the bonding mode of a number of polynuclear heteroaromatic nitrogen ligands with (η^5-pentamethylcyclopentadienyl)rhodium dicationic complexes (Cp^*Rh^{2+}), i.e., nitrogen (N) versus π-bonding, and have shown that the regioselectivity of nitrogen ring reduction is in fact dependent on the ligand being N-bonded to the Rh metal center.[2]

While we were in the process of carrying out a similar bonding and catalysis study with (η^5-cyclopenetadienyl)-ruthenium cation [$CpRu(S)_3^+$, S = CH_3CN],[3] Chaudret and Jalon published some preliminary results on the bonding mode of pyridine and several methyl-substituted pyridine ligands with (η^5-pentamethylcyclopentadienyl)ruthenium cation (Cp^*Ru^+).[4] In all cases, they isolated π-bonded complexes, while observing a pronounced solvent effect in acetone that provided a pyridine N-bonded complex [$(py)_6Ru^{2+}$], with a concomitant loss of Cp^*.

We wish to report our preliminary bonding results with $CpRu(CH_3CN)_3^+$ and ligands **1–7**, which are dramatically different than the bonding study reported (pyridine and substituted analogues) for Cp^*Ru^+ and, further, we report a novel N(η^1) to π(η^6) rearrangement for N-bonded $CpRu(2\text{-methylpyridine})(CH_3CN)_2^+$ (**9**), $CpRu(2,4\text{-dimethylpyridine})(CH_3CN)_2^+$ (**10**), and $CpRu(\text{quinoline})(CH_3CN)_2^+$ (**14**) to their π-bonded analogues **11**, **12**, and **15**, respectively.

The reaction of excess pyridine (**1**) with $CpRu(CH_3CN)_3^+$ (30 min at room temperature in CH_2Cl_2) provided complex **8**, which was clearly tris N-bound from ^{1}H and ^{13}C NMR and elemental analysis data.[5] More importantly, prolonged heating (12 h) of **8** in 1,2-dichloroethane at 80 °C provided no other product (^{1}H NMR).



8

The reaction of 2-methylpyridine (**2**) and 2,4-dimethylpyridine (**3**) with $CpRu(CH_3CN)_3^+$ also resulted in the formation of N-bonded complexes by ^{1}H NMR analysis. We were successful in isolating N-bonded complexes, **9** and **10** (R = CH_3, R_1 = H and R, R_1 = CH_3), by using short reaction times (5 min at room temperature in CH_2Cl_2), followed by addition of diethyl ether and crystallization (−30 °C) of the product.[6] Initial attempts to

(1) (a) Fish, R. H.; Thormodsen, A. D.; Cremer, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 5234. (b) Fish, R. H.; Tan, J. L.; Thormodsen, A. D. *J. Org. Chem.* **1984**, *49*, 4500. (c) Fish, R. H.; Tan, J. L.; Thormodsen, A. D. *Organometallics* **1985**, *4*, 1743.

(2) Fish, R. H.; Kim, H.-S.; Babin, J. E.; Adams, R. A. *Organometallics* **1988**, *7*, 2250.

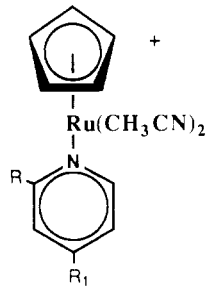
(3) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485.

(4) Chaudret, B.; Jalon, F. A. *J. Chem. Soc., Chem. Commun.* **1988**, 711.

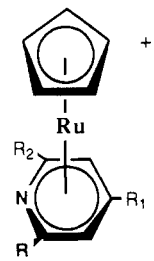
(5) Complex **8**: PF_6, 81%; ^{1}H NMR (500 MHz, $(CD_3)_2CO$, δ) Cp, 4.24 (s), H (2), 8.72 (dd, J = 6.4, 1.5 Hz), H(3), 7.46 (dd, J = 6.4, 7.5 Hz), H(4) 7.96 (tt, J = 1.5, 7.5 Hz); ratio, 5:2:2:1; ^{13}C{^{1}H} NMR ($(CD_3)_2CO$,δ) Cp, 70.90, C(1), 155.91, C(2), 126.52, C(3), 138.14. Anal. Calcd for $C_{20}H_{20}N_3Ru(PF_6)$: C, 43.80; H, 3.68; N, 7.66. Found: C, 43.53; H, 3.54; N, 7.40.

0276-7333/89/2308-1375$01.50/0 © 1989 American Chemical Society

isolate these above-mentioned N-bonded complexes by using longer reaction times (20 h at room temperature in CH_2Cl_2) followed by solvent removal only resulted in the isolation of the π-bonded complexes **11** and **12** (R = CH_3, R_1, R_2 = H and R, R_1 = CH_3, R_2 = H) and demonstrated the lability of the acetonitrile ligand.[7] It is interesting to note that **4**, 2,4,6-trimethylpyridine, only provided the π-bonded complex **13** (R, R_1, R_2 = CH_3), an indication that steric crowding around nitrogen prevents the ligand from N-bonding.[8]

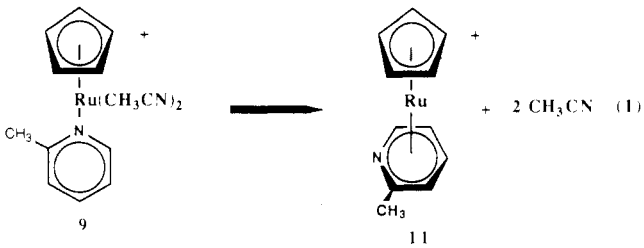


9,10



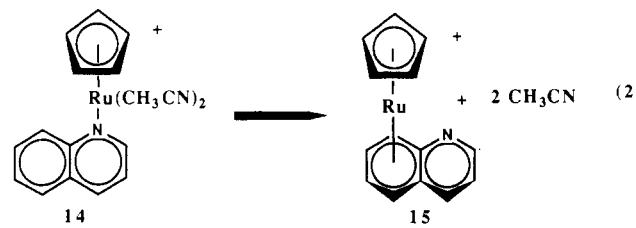
11-13

In the course of studying the thermal stability of **9** and **10** by variable-temperature (VT) ^1H NMR analysis, we discovered a novel and unprecedented N to π rearrangement occurring for both complexes. For example, complex **9** clearly showed (500 MHz ^1H NMR in 1,2-dichloroethane-d_4) that as the temperature was raised from 23 to 70 °C over a 1.5-h period, the formation of complex **11** was observed (ratio of **9**/**11** = 6:1 at 70 °C), *without the observation of free ligand* **2** (eq 1). As far as we have been able to determine, this type of N to π rearrangement has not been observed previously but possibly has some analogy to a $CpRu(PPh)_2(\eta^1$, S-thiophene)$^+$ to $\pi(\eta^5)$ rearrangement reported by Rauchfuss et al.[9]



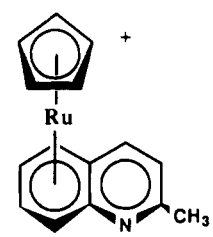
9 **11**

In order to ascertain whether this novel rearrangement was also prevalent in polynuclear heteroaromatic nitrogen ligand complexes, we studied the reaction of ligand **5**, quinoline, with $CpRu(CH_3CN)_3^+$. Both the N-bonded complex **14** and complex **15**, π-bonded to the benzene ring (η^6) rather than the pyridine ring (^{13}C NMR), were isolated by using the aforementioned procedures.[10] The N to π rearrangement of **14** to **15** was extremely facile and occurred on immediate dissolution of pure **14** in 1,2-dichloroethane-d_4. Upon heating the mixture of complexes **14** and **15** (**14**/**15** = 7:3) in an NMR tube (500-MHz ^1H NMR, 1,2-dichloroethane-d_4) from 23 to 70 °C over a 1.5-h period, we found that the ratio of **14**/**15** at 70 °C became 1:9 (eq 2). As in the VT NMR experiment with complex **9**, we saw no free ligand **5** in the N to π rearrangement of **14** to **15**.

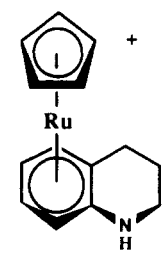


14 **15**

Two other ligands, 2-methylquinoline (**6**) and 1,2,3,4-tetrrahydroquinoline (**7**), were reacted with $CpRu(CH_3CN)_3^+$ to provide π-bonded (η^6) complexes, **16** and **17**.[11,12]



16



17

(6) Complex **9** (air and moisture sensitive): PF_6, 73%; ^1H NMR (500 MHz, 1,2-$C_2D_4Cl_2$, δ) Cp, 4.21 (s), H(6), 8.89 (s, br), H(4), 7.69 (t, br, J = 6.1 Hz), H(3), 7.37 (d, br, J = 7.6 Hz), H(5), 7.14 (s, br), CH_3, 2.83 (s, br), CH_3CN, 2.41 (s, br); ratio 5:1:1:1:1:3:6; $^{13}C\{^1H\}$ NMR (1,2-$C_2D_4Cl_2$, δ) Cp, 68.92, C(2), 163.70, C(6), 155.14, C(4), 137.37, C(3), 126.11, C(5), 121.81, CH_3, 27.56, CH_3CN, 3.99. Anal. Calcd for $C_{15}H_{18}N_3Ru(PF_6)$: C, 37.04; H, 3.73; N, 8.64. Found: C, 37.40; H, 3.80; N, 8.49. Complex **10** (air and moisture sensitive): PF_6, 100% (NMR); ^1H NMR (500 MHz, CD_2Cl_2, δ) Cp, 4.19 (s, br), H(6), 8.68 (s, br), H(3), 8.18 (s, br), H(5) 7.18 (s, br), 2-CH_3, 2.76 (s, br), CH_3CN, 2.46 (s, br), 4-CH_3, 2.35 (s, br); ratio 5:1:1:1:3:6:3. Correct analytical data for **10** could not be obtained because of its instability.

(7) Complex **11**: PF_6, 75%; ^1H NMR (500 MHz, $(CD_3)_2CO$, δ) Cp, 5.70 (s), H(6), 7.33 (m), H(4), 6.79 (m), H(3,5), 6.60 (m), CH_3, 2.64 (s); ratio, 5:1:1:2:3; $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ) Cp, 83.45, C(2), 121.83, C(6), 104.84, C(4), 89.79, C(3), 88.31, C(5), 85.18, CH_3, 22.60. Anal. Calcd for $C_{11}H_{12}NRu(PF_6)$: C, 32.68; H, 2.99; N, 3.46. Found: C, 32.74; H, 2.89; N, 3.27. Complex **12**: PF_6, 73%; ^1H NMR (500 MHz, $(CD_3)_2CO$, δ) Cp, 5.64 (s), H(6), 7.27 (dd, J = 3.8, 0.7 Hz), H(3), 6.83 (s), H(5), 6.61 (dd, J = 0.7, 3.8 Hz), 2-CH_3, 2.62 (s), 4-CH_3, 2.39 (s); ratio 5:1:1:1:3:3; $^{13}C\{^1H\}$-NMR ($(CD_3)_2CO$, δ) Cp, 83.46, C(2), 121.20, C(4), 106.80, C(6), 104.23, C(3) 87.77, C(5), 86.23, 2-CH_3, 22.38, 4-CH_3, 19.80. Anal. Calcd for $C_{12}H_{14}NRu(PF_6)$: C, 34.46; H, 3.37; N, 3.35. Found: C, 34.01; H, 3.55; N, 3.47.

(8) Complex **13**: PF_6, 63%; ^1H NMR (500 MHz, $(CD_3)_2CO$, δ) Cp, 5.57 (s), H(3 and 5), 6.68 (s), 2- and 6-CH_3, 2.60 (s), 4-CH_3, 2.36 (s); ratio 5:2:6:3; $^{13}C\{^1H\}$NMR ($(CD_3)_2CO$, δ), Cp, 83.47, C(2 and 6), 119.78, C(4), 106.20, C(3 and 5), 86.23, 2- and 6-CH_3, 22.31, 4-CH_3, 19.63. Anal. Calcd for $C_{13}H_{16}NRu(PF_6)$: C, 36.12; H, 3.73, N, 3.24. Found: C, 35.90, H, 3.61, N, 3.06.

(9) Draganjac, M.; Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1985**, *4*, 1909.

(10) Complex **14** (air and moisture sensitive): PF_6, 60%; ^1H NMR (500 MHz, CD_2Cl_2, δ) Cp, 4.29 (s), H(2), 9.35 (d, J = 5.1 Hz), H(3), 7.48 (dd, J = 5.1, 8.1 Hz), H(4), 8.32 (d, J = 8.1 Hz), H(5), 7.93 (d, J = 8.1 Hz), H(6), 7.66 (t, J = 8.5 Hz), H(7), 7.85 (t, J = 8.0 Hz), H(8), 8.81 (d, J = 8.8 Hz); CH_3CN, 2.35 (s); ratio 5:1:1:1:1:1:1:1:6; $^{13}C\{^1H\}$NMR (CD_2Cl_2, δ) Cp, 69.35, C(2), 157.39, C(3), 121.62, C(4), 138.53, C(5), 130.80, C(6), 127.55, C(7), 129.13, C(8), 131.09, C(9), 150.12, C(10), 129.83, CH_3CN, 4.08. Anal. Calcd for $C_{18}H_{18}N_3Ru(PF_6)$: C, 41.39; H, 3.47; N, 8.04. Found: C, 41.10; H, 3.43; N, 8.04. Complex **15**: PF_6, 100%; ^1H NMR (500 MHz, $(CD_3)_2CO$, δ) Cp, 5.24, H(2), 9.19 (dd, J = 1.7, 3.8 Hz), H(3), 7.66 (dd, J = 3.8, 8.9 Hz), H(4), 8.46 (dd, J = 1.1, 8.9 Hz), H(5), 7.24 (d, J = 5.9 Hz), H(6), 6.52 (dt, J = 0.6, 6.0 Hz), H(7), 6.63 (dt, J = 0.9, 6.0 Hz), H(8), 7.34 (d, J = 6.1 Hz); ratio 5:1:1:1:1:1:1:1; $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, δ) Cp, 81.21, C(2), 161.62, C(3), 126.34, C(4), 140.54, C(5), 88.43, C(6), 86.33, C(7), 84.87, C(8) 87.31, C(9), 94.05, C(10), 114.34. Anal. Calcd for $C_{14}H_{12}NRu(PF_6)$: C, 38.19; H, 2.75; N, 3.18. Found: C, 38.04; H, 2.76; N, 3.25.

(11) Complex **16**: PF_6, 85%; ^1H NMR (500 MHz, CD_2Cl_2, δ) Cp, 5.03, H(3), 7.37 (d, J = 9.0 Hz), H(4), 8.07 (d, J = 9.0 Hz); H(5), 7.05 (d, J = 6.3 Hz), H(6), 6.30 (dt, J = 1.0, 5.9 Hz), H(7), 6.19 (dt, J = 0.7, 6.1 Hz), H(8), 6.86 (d, J = 5.8 Hz); 2-CH_3, 2.68 (s); ratio 5:1:1:1:1:1:1:3; $^{13}C\{^1H\}$-NMR ($(CD_3)_2CO$, δ) Cp, 80.93, C(2), 171.10, C(3), 127.87, C(4), 140.0, C(5), 88.07, C(6), 85.60, C(7), 84.50, C(8), 86.66, C(9), 114.7, C(10), 92.09, 2-CH_3, 26.38. Anal. Calcd for $C_{15}H_{14}NRu(PF_6)$: C, 39.66; H, 3.11; N, 3.08. Found: C, 39.58; H, 3.11; N, 3.04. Complex **17**: PF_6, 91%; ^1H NMR (500 MHz, CD_2Cl_2, δ) Cp, 5.14 (s), H(2), 3.3(m), H(3,ax), 1.84 (m), H(3, eq), 2.08 (m), H(4,ax), 2.48 (m), H(4,eq), 2.67 (m), H(8), 5.78 (d, J = 5.5 Hz), H(7,5), 5.68 (m), H(6), 5.56 (dt, J = 1.0, 5.7 Hz); ratio 5:2:1:1:1:1:1:2:1; ^{13}C NMR (CD_3CN, δ) Cp, 79.87, C(2), 41.15, C(3), 21.47, C(4), 27.00, C(5–10), 81.20, 83.50, 85.15, 86.00, 86.89, 125.70. Anal. Calcd for $C_{14}H_{16}NRu(PF_6)$: C, 37.85; H, 3.63; N, 3.15. Found: C, 37.88; H, 3.61; N, 3.08.

(12) For an excellent review of the η^6 complexation of arenes, including substituted indole ligands, with $CpRu^+$ see: Moriarty, R. M.; Gill, U. S.; Ku, Y. Y. *J. Organomet. Chem.* **1988**, *350*, 157 and references therein.

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)

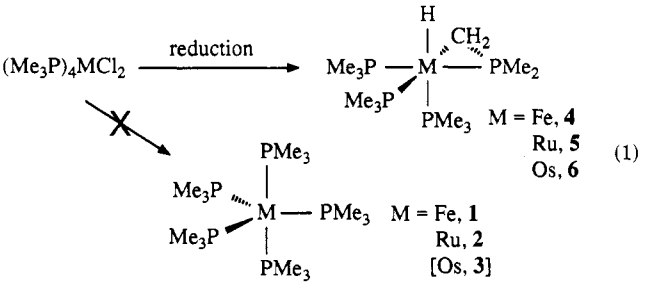
Susan P. Ermer, Ronald S. Shinomoto, Mark A. Deming, and Thomas C. Flood*

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

Received February 13, 1989

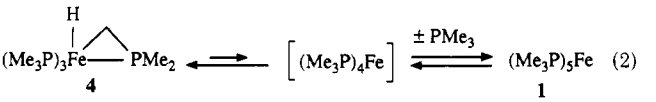
Summary: The new complex $(Me_3P)_5Os$ (**3**) has been prepared and characterized. It is nonrigid at ambient temperature on the NMR time scale. Treatment of **3** with triflic acid yielded $[(Me_3P)_5OsH]OTf$ (**7**). Thermolysis of **3** above 40 °C in neat THF, benzene, neohexene, tetramethylsilane, 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)

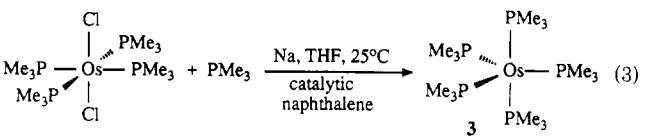
Schmidbaur[2] and Muetterties[3] prepared iron complex **4**. They found evidence for a facile, reversible reductive elimination and complexation by L (PMe_3) to form **1** in concentrations not directly detectable by NMR (eq 2).



(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.

0276-7333/89/2308-1377$01.50/0 © 1989 American Chemical Society