reagents $Ir(CO)(PPh_3)_2Cl$ and $H_2Os_3(CO)_{10}$. Although some new products have been obtained,[12] we did not observe the formation of I in any thermal reaction up to and including reaction in refluxing octane solvent.

Acknowledgment. This work was supported by the Office of Basic Energy Sciences of the U.S. Dept. of Energy under Contract No. DE-AC-2-78ER04900 and the Alfred P. Sloan Foundation through a fellowship to R.D.A. NMR studies were supported in part under Grant No. CHE-7916210 from the Chemistry Division of the National Science Foundation. We also thank Engelhard Industries for a load of osmium tetroxide.

Registry No. $Ir(N_2)(PPh_3)_2Cl$, 15695-36-0; $H_2Os_3(CO)_{10}$, 41766-80-7.

Supplementary Material Available: Tables of interatomic distances and angles, final positional and thermal parameters, and structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

---

[12] These are currently being characterized.

Cyclotantalation of 2,6-Di-*tert*-butylphenoxide[1]

Linda Chamberlain, Judy Keddington, and Ian P. Rothwell*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

John C. Huffman

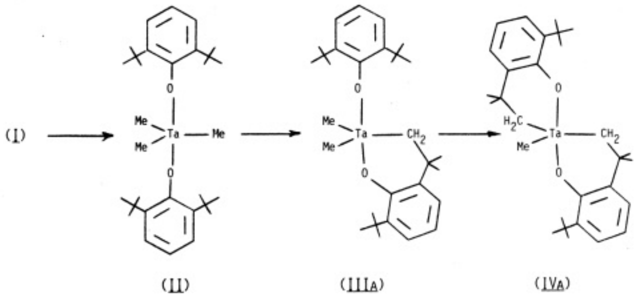
Molecular Structure Center, Indiana University
Bloomington, Indiana 47405

Received July 30, 1982

Summary: Alkylation of $Ta(OAr')_2Cl_3$ (OAr′ = 2,6-*tert*-butylphenoxide) followed by thermolysis leads to cyclometalation of the aryl oxide ligand in which one of the CH bonds of a *tert*-butyl group has been activated to cleavage.

Since the discovery of the first cyclometalation reaction by Kleinmann in 1963[2], a large number of such intramolecular, cyclic metalations have been reported.[3,4] Most known cyclometalation reactions are with ligands containing N of P-donor atoms reacting with low-valent group 7 or 8 metal systems to activate aromatic or benzylic type CH bonds, with a strong tendency to form five-membered chelate rings.[4] With trialkylphosphine ligands activation of purely aliphatic CH bonds has been seen, sometimes with the formation of four- or six-membered rings.[5] We wish to report here our characterization of a new type of cyclometalation reaction involving a high-valent, early transition-metal system in which the ligand contains an oxygen donor atom and involves the activation of an aliphatic CH bond to form a six-membered ring.[6]

Scheme I



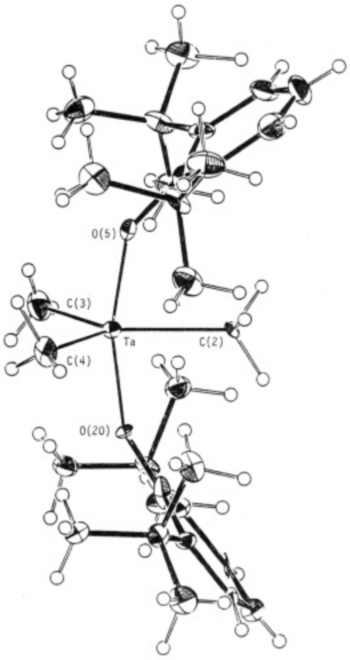


Figure 1. ORTEP view of II. Some pertinent bond distances (Å) and angles (deg) are Ta–O(5) = 1.930 (6), Ta–O(2) = 1.945 (6), Ta–C(2) = 2.248 (10), Ta–C(3) = 2.136 (10), Ta–C(4) = 2.138 (10), O(5)–Ta–O(20) = 164.1 (2), C(2) = 81.1 (3), –C(3) = 95.2 (3), C(4) = 95.2 (3), O(20)–Ta–C(2) = 83.0 (3), –C(3) = 95.0 (3), –C(4) = 94.1 (3), C(2)–Ta–C(3) = 127.0 (4), C(2)–Ta–C(4) = 128.3 (4), C(3)–Ta–C(4) = 104.7 (4).

Treatment of $TaCl_5$ with an excess of LiOAr′ (OAr′ = 2,6-di-*tert*-butylphenoxide) in benzene leads to the formation of $Ta(OAr')_2Cl_3$ (I) as an orange, hydrocarbon-soluble solid. Further substitution by LiOAr′ does not occur.[7] Alkylation of I with $LiCH_3$ at 25 °C in benzene leads to substitution of the chloride ligands and formation of $Ta(OAr')_2(Me)_3$ (II).[8] A single-crystal X-ray structure analyisis of this compound revealed an approximate tbp coordination geometry about the metal with equatorial methyl groups and axial aryl oxide ligands (vide infra). Thermolysis of II in toluene in a sealed tube (120 °C) leads to the generation of methane (2 equiv) and the formation of a new complex (IVa) in which each of the aryl oxide ligands has undergone attack on one of the CH bonds of

---

[1] The Chemistry of Sterically Crowded Aryl-Oxide Ligands. 2. For part 1, see: Chamberlain. L; Huffman, J. C.; Keddington, L.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.*, in press.

[2] Kleinmann, J. P.; Dubeck, M. *J. Am. Chem. Soc.* **1963**, *85*, 1544.

[3] De-hand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 326.

[4] Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73.

[5] Goel, R. G.; Ogini, W. O. *Organometallics* **1982**, *1*, 654.

[6] The observed attack on the CH bonds of the $N(SiMe_3)_2$ ligand can be considered to be a cyclometalation reaction, in which a four-membered ring is formed: Bennett, C. R.; Bradley, D. C. *J. Chem. Soc., Chem. Commun.* **1974**, 29. Simpson, S. J.; Turner, H. W.; Anderson, R. A. *Inorg. Chem.* **1981**, *20*, 2991.

[7] Anal. Calcd for $TaCl_3O_2C_{28}H_{42}$ (I): C, 48.19; H, 6.07; Cl, 15.24. Found: C, 48.82; H, 6.13; Cl, 14.98%.

[8] Anal. Calcd for $TaO_2C_{31}H_{51}$ (II): C, 58.48; H, 8.07. Found: C, 57.90; H, 7.96. ^1H NMR (benzene-d_6; 35 °C): $\delta(C_6H_3)$ 6.7–7.2 (m), δ $(C_6H_3\text{-}t\text{-}Bu_2)$ 1.45 (s), δ $(TaCH_3)$ 1.19 (s).

0276-7333/82/2301-1538$01.25/0

a *tert*-butyl group (Scheme I).[9] Carrying out the thermolysis in a ^1H NMR tube in toluene-d_8 allowed the reaction to be monitored and indicated the existence in solution of an intermediate, monocyclometalated compound (IIIa).

In contrast to the alkylation with $LiCH_3$, treatment of II with LiPh at 25 °C does not allow the isolation of a triphenyl compound but instead leads to a good yield of a monocyclometalated compound (IIIb).[10] Structural analysis of this compound confirmed the presence of the cyclometalated aryl oxide ligand (vide infra). Thermolysis of IIIb generates 1 equiv of benzene and the biscyclometalated compound IVb.[11]

Structure of II.[12] Figure 1 shows a view of the molecule with the atom numbering scheme used along with some pertinent bond distances and angles. The molecule can be seen to possess an approximately tbp geometry about the metal but with some very interesting distortions. The two axial aryl oxide ligands are arranged such that the molecule possesses C_{2v} symmetry with one of the methyl groups being unique. It can be seen that the two aryl oxide ligands are tilted toward this group with an O–Ta–O angle of 164.1°. This distortion results from an attempt to try and relieve the obvious steric congestion about the metal center and in particular the interaction between the four *tert*-butyl groups and the other two equatorial methyl groups, C(3) and C(4). The four *tert*-butyl groups thus surround the unique methyl group and this leads to a remarkable elongation of the Ta–C(2) bond length by 0.11 Å over that of Ta–C(3) and Ta–C(4). A compression of the C(3)–Ta–C(4) angle to 104.7° also takes place. Refinement of the hydrogen atoms shows that each of the *tert*-butyl groups contains a unique hydrogen atom that is situated very close to the Ta–C(2) function (Ta–H distances between 2.836 and 3.001 Å). These distances are too far to propose any positive electronic Ta···H interactions in the ground state, but when coupled with the long Ta–C(2) distance it strongly indicates a possible reaction pathway whereby loss of alkane can take place with formation of a new Ta–C bond as found in the structure of IIIb.

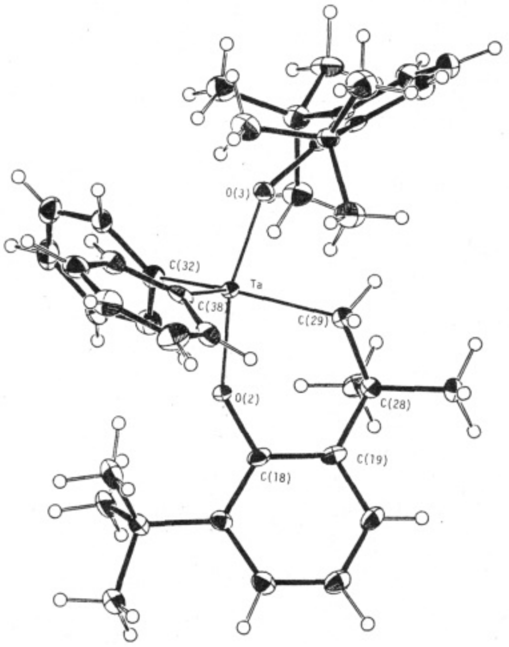


Figure 2. ORTEP view of IIIb. Some pertinent bond distances (Å) and angles (deg) Ta–O(2) = 1.909 (4), Ta–O(3) = 1.926 (4), Ta–C(29) = 2.158 (6), Ta–C(32) = 2.154 (6), Ta–C(38) = 2.145 (6), O(2)–Ta–O(3) = 165.4 (2), –C(29) = 80.72 (2), –C(32) = 89.8 (2), –C(38) = 90.1 (2), O(3)–Ta–C(29) = 84.7 (2), –C(32) = 98.9 (2), –C(38) = 97.2 (2), C(29)–Ta–C(32) = 128.5 (2), C(29)–Ta–C(38) = 117.6, and C(32)–Ta–C(38) = 112.9 (2).

Structure of IIIb.[13] Figure 2 contains a view of the molecule along with some pertinent bond distances and angles. The coordination geometry about the metal atom is very similar to that found in II with an equatorial plane of carbon atoms with two axial oxygen atoms bent toward the unique, metalated alkyl group (O–Ta–O = 165.4°). The six-membered chelate ring does not undergo a large amount of puckering and can best be described as a half-boat (or chair) in which the CMe_2 atom is lifted out of the plane of the other five atoms in the chelate ring. This results in an almost perfectly staggered geometry for the $C(Me)_2$–$C(H)_2$ substituents when viewed down the C–C axis. Surprisingly, the six-membered ring can still accommodate a chelate angle O(2)–Ta–C(29), of only 80.7° at the metal without undergoing a large amount of puckering. The reason for this is that the Ta–O(2)–C(18) angle is opened up to 143.7° and thus "tightens up" the chelate ring. This distortion is a common feature of early transition-metal alkoxide chemistry. It can be seen in both of the aryloxide ligands in II and in the unmetalated ligand in IIIb, where typical M–O–Ar angles are 144–150°. This angle increase is normally taken to imply that a degree of π-bonding between the electron-deficient metal center and the oxygen atom is taking place, but in the case of these sterically crowded aryl oxide ligands steric factors may be dominant. The ^1H NMR spectrum of IIIb is consistent with the solid-state structure.[10]

Structure of IV. At the present time a structural analysis of either IVa or IVb has not been carried out. However, the ^1H NMR spectra for these compounds is entirely consistent with the structure shown (Scheme I). We propose that the cyclotantalation of the second aryl oxide ligands does not lead to any drastic change in the coordination geometry from that seen in II and IIIb. The molecule has C_2 symmetry, and thus in a stereochemically rigid molecule the methylene protons of the chelate ring will become diastereotopic, generating an AB pattern. Similarly the $C(Me)_2$ groups will become nonequivalent. This pattern is observed for both IVa and IVb in the ^1H NMR spectrum.[9,11]

---

(9) A sample of II (0.5 g) was dissolved in toluene (10 mL) and the solution degassed, frozen to liquid-nitrogen temperatures, and sealed under vacuum in a glass tube. The tube was heated in an oil bath at 120 °C for 24 h. Removal of solvent followed by extraction with hexane gave a colorless solution from which could be isolated IVa as a white, crystaline solid in good yield (~350 mg). ^1H NMR (benzene-d_6; 30 °C) $\delta(C_6H_3)$ 6.8–7.4 (m), $\delta(C_6H_3\text{-}t\text{-}Bu)$ 1.76 (s), $\delta(C_6H_3CMe_2CH_2)$ 1.28 (s), 1.35 (s), $\delta(C_6H_3CMe_2CH_2)$ AB pattern at 1.74–1.80 obscurred partly by *t*-Bu signal, $\delta(TaCH_3)$ 0.91 (s).

(10) Addition of LiPh (3.3 equiv) to a solution of I in benzene gave a dark solution after 2 h at 25 °C. Removal of solvent followed by extraction with hexane gave a colorless solution which deposited colorless crystals of IIIb on cooling to −15 °C. ^1H NMR (benzene-d_6; 30 °C): $\delta(C_6H_3)$ and δ(TaPh) 6.9–8.1 (m), $\delta(C_6H_3\text{-}t\text{-}Bu_2)$ 1.24 (s), $\delta(C_6H_3\text{-}t\text{-}BuCMe_2CH_2)$ 0.96 (s), $\delta(C_6H_3\text{-}t\text{-}BuCMe_2CH_2)$ 1.42 (s) $\delta(C_6H_3\text{-}t\text{-}CMe_2CH_2)$ 2.21 (s).

(11) A similar thermolysis procedure[9] carried out on IIIb led to the isolation of IVb as a white crystalline solid. ^1H NMR (benzene-d_6; 30 °C): $\delta(C_6H_3)$ and δ(TaPh) 6.9–8.1 (m), $\delta(C_6H_3\text{-}t\text{-}Bu)$ 1.57 (s), $\delta(C_6H_3CMe_2CH_2)$ 1.28 (s), 1.32 (s), $\delta(C_6H_3CMe_2CH_2)$ 2.27 (d), 1.60 (d).

(12) *Crystal data* for $Ta(CH_3)_3(C_6H_3\text{-}t\text{-}Bu_2)_2$ at −162 °C: space group C_2, $a = 19.797$ (4), Å, $b = 6.587$ (7) Å, $c = 23.253$ (5) Å, $\beta = 96.11$ (1)°, $Z = 4$, $d_{calcd} = 1.403$ g cm.$^{-3}$ Of the 2173 unique reflections collected with use of Mo Kα radiation, $6° \leq 2\theta \geq 45°$, the 1995 having $F < 2.33\,\sigma(F)$ were used in the full-matrix refinement. Final residuals are $R(F) = 0.0258$ and $R_w(F) = 0.0245$.

(13) *Crystal Data* for $TaC_{40}H_{57}O_2$ at −162 °C: space group $P\bar{1}$, $a = 15.438$ (6) Å, $b = 12.329$ (4) Å, $c = 10.639$ (3) Å, $\alpha = 73.70$ (2)°, $\beta = 67.38$ (2), $\gamma = 69.07$ (2)°, $Z = 2$, d_{calcd} 1.437 g cm^{-3}. Of the 4521 unique reflections collected with use of Mo Kα radiation, $6° \leq 20 \leq 45°$, the 4089 having $F < 2.33\,\sigma(F)$ were used in the full-matrix refinement. Final residuals are $R(F) = 0.0322$ and $R_w(F) = 0.0318$.

Further studies of this interesting reaction are in progress.[14]

Registry No. I, 82190-58-7; II, 82182-23-8; IIIb, 82823-96-9; IVa, 82823-97-0; IVb, 82823-98-1; $TaCl_5$, 7721-01-9; LiOAr′, 55894-67-2; $LiCH_3$, 917-54-4; LiPh, 591-51-5.

Supplementary Material Available: Tables of bond angles, bond distances, fractional coordinates and isotropic thermal parameters, and anisotropic thermal parameters for IIIb (11 pages). Ordering information is given on any current masthead page.

---

(14) We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support.

Ancillary Ligand Rearrangements Promoted by the Migratory Insertion of Carbon Monoxide into Nickel(II)–Carbon Bonds

Michael D. Fryzuk* and Patricia A. MacNeil

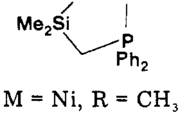
Department of Chemistry, University of British Columbia
Vancouver, British Columbia, Canada V6T 1Y6

Received May 24, 1982

Summary: Migratory insertion of CO into the nickel(II) carbon bonds of $[Ni(R)N(SiMe_2CH_2PPh_2)_2]$ promotes a rearrangement of the amidophosphine hybrid ligand to generate a nickel(0) dicarbonyl derivative, $[Ni(CO)_2\{RCON(SiMe_2CH_2PPh_2)_2\}]$. With the palladium-methyl derivative $[Pd(CH_3)N(SiMe_2CH_2PPh_2)_2]$, only the palladium(II) acetyl complex $[Pd(COCH_3)N(SiMe_2CH_2PPh_2)_2]$ is formed with no evidence of anicillary ligand rearrangement.

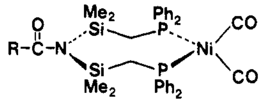
Our approach to fine-tuning the reactivity patterns of a given transition-metal complex involves the use of ancillary multidentate ligands that contain vastly different donor atom types. Up to the present we have investigated the coordination chemistry of bidentate and tridentate "hybrid" ligands containing the *hard* amido donor NR_2^- (R = alkyl or silyl) and *soft* phosphine donors with a number of different transition metals.[1,2] The primary purpose of these "hybrid" ligands is to provide new electronic and steric environments for a given metal while being inert to further transformations at the metal center; however, we have found that in certain cases, notably nickel(II), this type of ligand system is noninnocent and undergoes a dramatic rearrangement.

We have previously reported[1b] the synthesis of organonickel and organopalladium derivatives (1) containing the uninegative, tridentate ligand $N(SiMe_2CH_2PPh_2)_2$. All of the organonickel complexes (**1a–d**) react[3] with carbon monoxide at atmospheric pressure to form new products that involve a change in formal oxidation state of the metal as well as a change in the chelating mode of the "hybrid" ligand.



1a, M = Ni, R = CH_3
b, M = Ni, R = η^3-C_3H_5
c, M = Ni, R = $CH{=}CH_2$
d, M = Ni, R = C_6H_5
e, M = Pd, R = CH_3

When gold-orange solutions of the nickel-methyl complex **1a** are exposed to CO under ambient conditions, the color fades over a period of 5 min to produce a new, single compound (**2a**) in quantitative yield (by ^1H NMR spectroscopy) with the overall uptake of 3 equiv of CO. *Colorless* crystals of **2a** can be isolated in 90% yield; analytical and solution molecular weight data are consistent with the monomeric empirical formula $[Ni(CH_3)N(SiMe_2CH_2PPh_2)_2(CO)_3]$.[4] The solution infrared spectrum of **2a** consists of two very strong terminal carbonyl bands at 1995 and 1930 cm^{-1} (which shift to 1955 and 1890 cm^{-1} with ^{13}CO) and a strong band at 1715 cm^{-1} (which shifts to 1680 cm^{-1} with ^{13}CO). **2a** is formulated as a nickel(0) dicarbonyl derivative wherein the ligand binds in a bidentate mode through the phosphine donors because of the formation of an *N*-acetyl group. Consistent with this proposal are the $^{13}C\{^1H\}$ NMR data that have a singlet at 161.9 ppm for the amide carbonyl carbon (Si_2NCOCH_3) and a triplet ($^2J_{^{31}P-^{13}C}$ = 2.4 Hz) for the terminal carbonyl ligands at 200.2 ppm. An identical reaction obtains for the allylnickel derivative **1b** to give **2b** as the only observed product,[5] once again as colorless crystals in 80% recrystallized yield. The key evidence for this type of structure is the acyl band in the IR spectrum at 1715 cm^{-1} which indicates an *amide*-type carbonyl rather than a nickel–acyl species.



2a, R = CH_3
b, R = $CH_2CH{=}CH_2$
c, R = $CH{=}CH_2$
d, R = C_6H_5

To test the generality of this reaction, the migratory insertion behavior of the sp^2-carbon ligands, vinyl ($CH{=}CH_2$) and phenyl (C_6H_5), was investigated.[6] The analogous reaction of CO with the vinylnickel complex **1c** proceeds

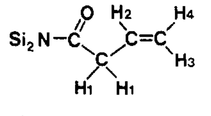
---

(1) (a) Fryzuk, M. D.; MacNeil, P. A. *J. Am. Chem. Soc.* **1981**, *103*, 3592. (b) Fryzuk, M. D.; MacNeil, P. A., Rettig, S. J.; Secco, A. S.; Trotter, J. *Organometallics* **1982**, *1*, 918.

(2) Fryzuk, M. D.; Williams, H. D.; Rettig, S. J., submitted for publication in *Inorg. Chem.* Zirconium and hafnium complexes of hybrid multidentate ligands are described.

(3) All reactions with CO and ^{13}CO (90% ^{13}C) were performed at 1 atm of pressure at room temperature in dry toluene. Typically, ~0.2 mol L^{-1} solutions of the nickel complexes **1** were rapidly stirred under carbon monoxide for the indicated times. The toluene was removed under vacuum and the residue recrystallized from hexanes at −30 °C.

(4) **2a**: mp 122 °C; mol wt (Signer), theoretical 689 found, 698; ^1H NMR (C_6D_6) $SiCH_3$, δ −0.11 (s), CH_2P, 1.89 (br d), $COCH_3$, 1.91 (s), $P(C_6H_5)$, 6.95 (m, para/meta), 7.53 (m, ortho). Anal. Calcd for $C_{34}H_{39}NNiO_3P_2Si_2$: C, 59.48; H, 5.68; N, 2.04. Found: C, 59.30; H, 5.73; N, 1.80.



(5) **2b**: mp 138–140 °C; ^1H NMR (C_6D_6) $SiCH_3$, δ −0.10 (s), CH_2P, 1.84 (br dd), H_1, 3.08 (dt, 2, $J_{1,2}$ = 6.59, $J_{1,3}$ = $J_{1,4}$ = 1.46 Hz), H_2, 5.85 (m, 1, $J_{2,4}$ = 10.01, $J_{2,3}$ = 17.09 Hz), H_3, 5.02 (m, 1, $J_{3,4}$ = 1.71 Hz), H_4, 4.85 (m, 1), $P(C_6H_5)$, 6.95 (m, para/meta), 7.52 (m, ortho). Anal. Calcd for $C_{36}H_{41}NNiO_3P_2Si_2$: C, 60.67; H, 5.76; N, 1.97. Found: C, 60.66; H, 5.89; N, 1.80.

(6) Although migratory insertion of CO into nickel–carbon bonds is well-known, the relative migratory aptitudes of alkyl, aryl, and vinyl derivatives of nickel have not yet been established. See, for example: (a) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 2524. (b) Stroppioni, P.; Dapporto, P.; Sacconi, L. *Inorg. Chem.* **1978**, *17*, 718. (c) Carmona, E.; Gonzalez, F.; Poveda, M. L.; Atwood, J. L.; Rogers, R. L. *J. Chem. Soc., Dalton Trans.* **1980**, 2108. (d) Tremont, S. J.; Bergman, R. G. *J. Organomet. Chem.* **1977**, *140*, C12.

0276-7333/82/2301-1540$01.25/0