mmol) also in the same solvent. The reaction mixture was stirred at 25 °C for 2 h before the solvent was removed in vacuo to yield an analytically pure dichloromethane solvate of **10** (yield, after washing with hexane (5 mL), 0.43 g, 95%; yellow microcrystalline; mp 165 °C dec). Anal. Calcd for $C_{31}H_{35}Cl_3NOAsPRhSi$: C, 47.68; H, 4.48; N, 1.79; Cl, 13.63. Found: C, 47.65; H, 4.46; N, 1.77; Cl, 13.60. ^1H NMR ($CDCl_3$): phenyl rings δ 7.35, 7.55, 7.70 (m, 20 H); As*CH*$_2$*CH*$_2$P δ 2.17 (m, 2 H), 2.60 (m, 2 H); $Si(CH_3)_3$ δ 0.05 (s, 9 H). ^{29}Si NMR (INEPT; $CDCl_3$): δ 6.20 (d, 1 Si, $^2J_{P^VSi}$ = 5.50 Hz).

(b) The Metallacycles $\overline{\mathrm{N{=}PPh_2(CH_2)_2AsPh_2Rh}}$(cod) (11) and $\overline{\mathrm{N{=}PPh_2(CH_2)_2AsPh_2Ir}}$(cod) (12) were prepared by employing similar experimental conditions to those described above for **10**.

11·CH_2Cl_2: yield 82%; yellow microcrystalline; mp 170 °C dec. Anal. Calcd for $C_{35}H_{38}Cl_2NAsPRh$: C, 55.87; H, 5.05; N, 1.86; Cl, 9.43. Found: C, 55.85; H, 5.01; N, 1.84; Cl, 9.49. ^1H NMR ($CDCl_3$) phenyl rings δ 7.37, 7.60, 7.80 (m, 20 H); As*CH*$_2$*CH*$_2$P δ 2.25 (m, 2 H), δ 2.65 (m, 2 H); cod olefinic δ 5.30 (br, 2 H), 5.45 (br, 2 H); cod methylene δ 2.30 (br, 4 H), 1.70 (br, 4 H).

12·CH_2Cl_2: yield 85%; brown microcrystalline; mp 190 °C dec. Anal. Calcd for $C_{35}H_{38}Cl_2NAsPIr$: C, 49.93; H, 4.52;, N, 1.66; Cl, 8.43. Found: C, 50.01; H, 4.49; N, 1.65; Cl, 8.46. ^1H NMR ($CDCl_3$): phenyl rings δ 7.35, 7.62, 7.85 (m, 20 H); As*CH*$_2$*CH*$_2$P δ 2.19 (m, 2 H), 2.60 (m, 2 H); cod olefinic δ 5.32 (br, 2 H), 5.40 (br, 2 H); cod methylene δ 2.30 (br, 4 H), 1.72 (br, 4 H).

Reactions of $Ph_3P{=}NSiMe_3$ (15) or $(Me_3SiN{=}PPh_2)_2CH_2$ (16) with $[M(cod)Cl]_2$ (M = Rh or Ir). The reactions were carried out under similar experimental conditions as described for **4** using equimolar quantities of **15** or **16** and $[M(cod)Cl]_2$ (M = Rh or Ir). The spectroscopic (^{31}P NMR) analysis of the reaction mixture clearly showed that no reaction had occurred, and the unreacted phosphoranes **15** and **16** were recovered almost quantitatively.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for support. We are also indebted to Dr. T. T. Nakashima, Mr. T. Brisbane, and Mr. G. Bigam for the NMR spectroscopy.

Registry No. 1, 116467-64-2; 2, 121498-15-5; 3, 121498-16-6; 4, 121498-17-7; 5, 121524-38-7; 6, 121498-14-4; 7, 121524-39-8; 8, 121498-21-3; 9, 121445-48-5; 10, 121498-18-8; 11, 121498-19-9; 12, 121498-20-2; 13, 116563-61-2; 14, 116563-62-3; 15, 13892-06-3; 16, 53380-82-8; $W(CO)_6$, 14040-11-0; $Mo(CO)_4(pip)_2$, 59967-36-1; $[Ir(cod)Cl]_2$, 12112-67-3; $[Rh(CO)_2Cl]_2$, 14523-22-9; Me_3SiN_3, 4648-54-8; $Ph_2P(CH_2)_2AsPh_2$, 23582-06-1; $[Rh(cod)Cl]_2$, 12092-47-6; pentafluorobenzonitrile, 773-82-0; pentafluoropyridine, 700-16-3.

Early–Late Transition Metal Bonds: Ruthenium–Titanium Compounds with Aryloxide Ligands

William J. Sartain and John P. Selegue*[†]

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055

Received January 23, 1989

$[RuH(CO)_2(Cp)]$ reacts with $[Ti(2,6\text{-}Me_2C_6H_3O)(NMe_2)_3]$ (1) and $[Ti(2,6\text{-}Me_2C_6H_3O)_2(NMe_2)_2]$ (2) to produce $[(NMe_2)_2(2,6\text{-}Me_2C_6H_3O)TiRu(CO)_2(Cp)]$ (3) and $[(NMe_2)(2,6\text{-}Me_2C_6H_3O)_2TiRu(CO)_2(Cp)]$ (4), respectively. Both products were characterized spectroscopically, and the structure of 4 was determined by an X-ray diffraction study. Compound 4 crystallizes in the space group $P2_1/n$ with a = 8.201 (3) Å, b = 18.776 (4) Å, c = 16.739 (6) Å, β = 103.90 (3)°, and V = 2526.29 Å^3. Full-matrix least-squares refinement converged at R = 5.6% and R_w = 6.5%. There is a direct, unbridged bond between titanium and ruthenium in 4, with a metal–metal bond length of 2.573 (1) Å. Despite steric crowding in 4, this Ru–Ti distance is 0.09 Å shorter than the Ru–Ti distance in $[(NMe_2)_3TiRu(CO)_2(Cp)]$, attributed in part to the weaker electron-donor ability of aryloxides.

Heterometallic compounds incorporating both early and late transition metals are of current interest due to their relationship to heterogeneous Fischer–Tropsch catalysts. Most of these catalysts consist of low-valent late transition metals supported on high-valent, electropositive metal or nonmetal oxides. The degree of interaction between the metal and its support has profound effects on the activity of the resulting catalyst. The term "strong metal-support interaction" (SMSI) was first used to describe the drastic decreases in the ability of noble metals of periodic groups 8–10 to chemisorb hydrogen when they are supported on titanium oxide. Later, the term was extended to cover a wider range of physicochemical effects on late transition metals supported on early-transition-metal oxides.[1] Indeed, the selectivity of Fischer–Tropsch catalysts for production of hydrocarbons, methanol, or C_2 and higher oxygenates is largely determined by the extent of interaction between the "active" metal and its promoters and/or support.[2] These effects are especially pronounced for noble metals on titanium, zirconium, vanadium, niobium, manganese, and lanthanum oxides. Tauster has recently suggested that SMSI effects result from *direct* interactions of reduced titanium ions (Ti^{3+}) in the support with the group 8–10 metals. This proposal is consistent with extended X-ray absorption fine structure (EXAFS) analysis of rhodium–titania catalysts and other spectroscopic data.[1a]

We are interested in preparing compounds which contain an early transition metal surrounded by "hard", π-donor ligands directly bound to a late transition metal surrounded by "soft", π-acceptor ligands, as models for catalysts which display SMSI. Heterometallic compounds have been the subject of several recent reviews, and it is evident that the majority of the transition-metal compounds contain bonds between low-valent late transition

---

[†] Alexander von Humboldt Fellow, 1987–1988.

(1) (a) Tauster, S. J. *Acc. Chem. Res.* **1987**, *20*, 389–394. (b) Imelik, B., Naccache, C., Coudurier, G., Praliaud, H., Meriaudeau, P., Gallezot, P., Martin, G. A., Verdrine, J. C., Eds. *Metal-Support and Metal-Additive Effects in Catalysis*; Elsevier: New York, 1982. (c) Iwasawa, Y.; Sato, H. *Chem. Lett.* **1985**, 507.

(2) Lee, G. v. d.; Ponec, V. *Catal. Rev.—Sci. Eng.* **1987**, *29*, 183–218.

0276-7333/89/2308-2153$01.50/0

metals with carbonyl, cyclopentadienyl, or closely related ancillary ligands.[3,4] Compounds with both late and early metals often utilize bridging ligands such as phosphides (μ-PR$_2$) to hold those metals together.[4] Such bridges have the advantage of producing stable compounds in which two different metals are forced to stay in the proximity of one another. Unfortunately, it is often difficult to judge the true strength of metal–metal interactions when strongly bridging ligands are also present.[5] For this reason, compounds with direct, unbridged bonds between early and late transition metals should provide more meaningful information about how these metals influence one another's properties.

In principle, each metal center in such binuclear compounds could undergo reactions characteristic of a mononuclear transition-metal compound. That is, a high-valent early metal could be active in processes such as alkene oxidation or metathesis, while an adjacent low-valent late metal could display oxidative addition, reductive elimination, and insertion reactions. Both kinds of processes play important roles in catalysis. In addition, the proximity of the two metal centers introduces the possibility of new modes of reactivity such as the formation and breaking of metal–metal bonds, activation of substrates as bridging ligands, cleavage of substrate covalent bonds, insertion into metal–metal bonds, and ligand mobility.

Older methods of preparing heterometallic bonds entailed reacting monometallic precursors under harsh conditions. Unfortunately, this method lacks predictability and usually gives numerous side products and low yields.[3] Displacement of an anionic or neutral ligand by an anionic metal complex is a more selective method, but it is limited mainly to carbonylmetallates as anions, and it is often plagued by oxidation–reduction side reactions. Nonetheless, Schmid and co-workers prepared [(Cp)Ti{Co(CO$_4$)}{(μ-OC)Co$_3$(CO)$_9$}$_2$], which contains a Ti–Co bond, by reacting [TiCl$_3$(Cp)] with Na[Co(CO)$_4$].[6] Casey and co-workers reacted K[M(CO)$_2$(Cp)] (M = Fe, Ru) with [ZrClX(Cp)$_2$] or [ZrI$_2$(Cp)$_2$] to form [(Cp)(CO)$_2$MZrX(Cp)$_2$] (X = Cl, OCMe$_3$, Me, Ru(CO)$_2$(Cp)) with unbridged Zr–Ru and Zr–Fe bonds.[7] Marks and co-workers made analogous [(Cp)(CO)$_2$RuThX(Cp)$_2$] (X = Cl, I) in this manner.[8] Numerous ligand-bridged bimetallic compounds have also been made by salt eliminations.[4,9]

Another selective approach to the formation of heterometallic metal–metal bonds is small molecule elimination.[3] Caulton and co-workers have used amine and methane eliminations as well as halide displacement to form hydride-bridged Rh–Zn,[10] Re–Zr, Os–Zr,[11] and Re–Al[12] compounds. Warner and Norton have formed numerous bimetallic compounds by binuclear aldehyde elimination reactions between an alkyl transition-metal carbonyl and a transition-metal hydride.[13] Bercaw and co-workers have utilized dihydrogen elimination as a method of making species with Zr–Ru, Zr–Co, and Zr–Rh bonds.[14]

Our approach to the synthesis of heterometallic metal–metal bonds is amine elimination between an early-transition-metal amide and a late-transition-metal hydride, which proceeds with loss of a secondary amine to give a heterometallic product with a direct metal–metal bond or an isocarbonyl bridge.[15] We have reported the synthesis of compounds containing Ti–Ru[16] and Ti–Fe[17] bonds by this route. Here we report the extension of this procedure to titanium amides with aryloxide ligands, which permitted us to examine the effects of ancillary ligand variations on early–late transition-metal bonds.

Experimental Section

All manipulations were carried out under a dry, oxygen-free nitrogen atmosphere, using either standard Schlenk techniques or a Vacuum Atmospheres glovebox. All solvents were dried over molecular sieves, then distilled under nitrogen from potassium or sodium benzophenone ketyl, and stored under nitrogen until use. Dicyclopentadiene was cracked to cyclopentadiene by distillation under nitrogen immediately before use. [TiCl$_4$] (Fisher Scientific Inc.), C$_6$D$_6$ (sealed vials from Stohler Isotope Chemicals or Cambridge Isotope Laboratories), and other reagents were used as received. [Ru$_3$(CO)$_{12}$],[18] [RuH(CO)$_2$(Cp)],[19] [Ti(NMe$_2$)$_4$][20] were prepared by literature methods.

IR spectra were recorded in isooctane solutions by using a Bomem DA3.02 interferometer at 1 cm^{-1} resolution. All ^{1}H NMR spectra were recorded at ambient temperature in C$_6$D$_6$ solution with C$_6$D$_5$H as an internal reference, using a Varian EM-390 spectrometer (90 MHz). Electron-impact mass spectra were recorded on a VG ZAB-2F mass spectrometer with an ionization voltage of 70 eV. Mass spectral data are reported by using the most intense peak in each isotope pattern and in all cases correspond to the calculated pattern. Melting points were measured in sealed capillaries under vacuum and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory.

Preparation of [Ti(2,6-Me$_2$C$_6$H$_3$O)(NMe$_2$)$_3$] (1). A solution of 2,6-Me$_2$C$_6$H$_3$OH (0.546 g, 4.48 mmol) in toluene (10 mL) was added dropwise to a solution of [Ti(NMe$_2$)$_4$] (1.00 g, 4.47 mmol) in toluene (50 mL). The clear orange solution was stirred for 2 h at room temperature and then evaporated under vacuum to an orange liquid. The NMR spectrum of this liquid indicated that it was pure [Ti(2,6-Me$_2$C$_6$H$_3$O)(NMe$_2$)$_3$]. ^{1}H NMR: δ 7.10 (mult, 3 H, C$_6$$H_3Me_2$), 3.07 (s, 18 H, NMe$_2$), 2.37 (s, 6 H, C$_6H_3$$Me_2$).

Preparation of [Ti(2,6-Me$_2$C$_6$H$_3$O)$_2$(NMe$_2$)$_2$] (2). Solid 2,6-Me$_2$C$_6$H$_3$OH (1.09 g, 8.93 mmol) was added over ca. 30 min to a solution of [Ti(NMe$_2$)$_4$] (1.00 g, 4.47 mmol) in toluene (50 mL). After being stirred at room temperature for 2 h, the clear, yellow-orange solution was evaporated under vacuum to an orange

---

(3) (a) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 6, Chapter 40. (b) Gladfelter, W. L.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1980**, *18*, 207. (c) Bruce, M. I. *J. Organomet. Chem.* **1985**, *283*, 339.

(4) (a) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167–173. (b) Gelmini, L.; Stephan, D. W. *Organometallics* **1988**, *7*, 849. (c) White, G. S.; Stephan, D. W. *Organometallics* **1988**, *7*, 903. (d) Targos, T. S.; Rosen, R. P.; Whittle, R. R. *Inorg. Chem.* **1985**, *24*, 1375. (e) Baker, R. T.; Tulip, T. H.; Wreford, S. S. *Inorg. Chem.* **1985**, *24*, 1379.

(5) (a) Ritchey, J. M. Zozulin, A. J.; Wrobleski, D. A.; Ryan, R. R.; Wasserman, H. J.; Moody, D. C.; Paine, R. T. *J. Am. Chem. Soc.* **1985**, *107*, 501–503. (b) Hay, P. J.; Ryan, R. R.; Salazar, K. V.; Wrobleski, D. A.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1986**, *108*, 313–315. (c) Ortiz, J. V. *J. Am. Chem. Soc.* **1986**, *108*, 550–551.

(6) Schmid, G.; Stutte, B.; Boese, R. *Chem. Ber.* **1978**, *111*, 1239.

(7) (a) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665. (b) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *Organometallics* **1984**, *3*, 504.

(8) (a) Sternal, R. B.; Brock, C. P.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8270–8272. (b) Sternal, R. B.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7920–7921.

(9) Casey, C. P.; Nief, F. *Organometallics* **1985**, *4*, 1218.

(10) Geerts, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1986**, *25*, 590.

(11) Bruno, J. W.; Huffman, J. C.; Green, M. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 8310.

(12) Skupinski, W. A.; Huffman, J. C.; Bruno, J. W.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 8128.

(13) Warner, K. E.; Norton, J. R. *Organometallics* **1985**, *4*, 2150.

(14) (a) Barger, P. T.; Bercaw, J. E. *J. Organomet. Chem.* **1980**, *201*, C39. (b) Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278.

(15) Sartain, W. J.; Selegue, J. P. *Organometallics* **1984**, *3*, 1922.

(16) Sartain, W. J.; Selegue, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 5818.

(17) Sartain, W. J.; Selegue, J. P. *Organometallics* **1987**, *6*, 1812.

(18) Eady, C. R.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Dalton Trans.* **1980**, 383.

(19) Humphries, A. P.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1710.

(20) (a) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857. (b) Made analogously to [Ti(NEt$_2$)$_4$]: Reetz, T. M.; Urz, R.; Schuster, T. *Synthesis* **1983**, 540.

liquid. The NMR spectrum of this liquid indicated that it consisted of ca. 75% $[Ti(2,6\text{-}Me_2C_6H_3O)_2(NMe_2)_2]$ and ca. 25% $[Ti(2,6\text{-}Me_2C_6H_3O)_3(NMe_2)]$. Efforts to achieve further purification by fractional distillation were unsuccessful. ^1H NMR: δ 7.00 (mult, $C_6\mathit{H}_3Me_2$), 3.10 (s, NMe_2 of $[Ti(2,6\text{-}Me_2C_6H_3O)_3(NMe_2)]$), 3.03 (s, NMe_2 of $[Ti(2,6\text{-}Me_2C_6H_3O)_2(NMe_2)_2]$), 2.27 (s, $C_6H_3\mathit{Me}_2$).

Preparation of $[Ti(2,6\text{-}Me_2C_6H_3O)_3(NMe_2)]$. Solid $2,6\text{-}Me_2C_6H_3OH$ (1.63 g, 13.4 mmol) was added over 30 min to $[Ti(NMe_2)_4]$ (1.00 g, 4.47 mmol) in toluene (50 mL). After 2 h, volatiles were evaporated under vacuum to yield an orange liquid. This liquid was redissolved in toluene (ca. 10 mL) and pentane was added until the solution became cloudy. Chilling to −40 °C yielded an orange solid. The NMR spectrum of this solid indicated that it was ca. 80% $[Ti(2,6\text{-}Me_2C_6H_3O)_3(NMe_2)]$ and ca. 20% $[Ti(2,6\text{-}Me_2C_6H_3O)_2(NMe_2)_2]$. Two additional recrystallizations from toluene/pentane failed to purify this mixture any further. ^1H NMR: δ 6.91 (mult, $C_6\mathit{H}_3Me_2$), 3.10 (s, NMe_2 of $[Ti(2,6\text{-}Me_2C_6H_3O)_3(NMe_2)]$), 3.03 (s, NMe_2 of $[Ti(2,6\text{-}Me_2C_6H_3O)_2(NMe_2)_2]$), 2.27 (s, $C_6H_3\mathit{Me}_2$).

Preparation of $[Ti\{2,6\text{-}(CMe_3)_2C_6H_3O\}_2(NMe_2)_2]$. Solid $2,6\text{-}(CMe_3)_2C_6H_3OH$ (1.84 g, 8.93 mmol) was slowly added to $[Ti(NMe_2)_4]$ (1.00 g, 4.47 mmol) in toluene (40 mL). After 2 h, the volatiles were evaporated under vacuum to yield a sticky solid. Trituration with several 10-mL portions of pentane afforded the product as an orange solid: yield 2.17 g (3.97 mmol, 89%); ^1H NMR δ 7.07 (mult, 6 H, C_6H_3), 3.08 (s, 12 H, NMe_2), 1.31 (s, 36 H, CMe_3).

Preparation of $[(NMe_2)_2(2,6\text{-}Me_2C_6H_3O)TiRu(CO)_2(Cp)]$ (3). A solution of $[RuH(CO)_2(Cp)]$ made from $[Ru_3(CO)_{12}]$ (0.1142 g, 0.1786 mmol) and cyclopentadiene (1.0 mL) in heptane (50 mL) was added to $[Ti(2,6\text{-}Me_2C_6H_3O)(NMe_2)_3]$ (1, 0.145 g 0.482 mmol) in heptane (10 mL). The resulting yellow solution was stirred for about 15 h at room temperature and then evaporated under vacuum to an oil. The oil was extracted with heptane (ca. 10 mL), and the extract was concentrated to the verge of cloudiness. Chilling at −40 °C afforded the product as yellow microcrystals: yield 0.097 g (0.20 mmol, 41%); mp 59–62 °C dec.); ^1H NMR δ 7.02 (mult, 3 H, $C_6\mathit{H}_3Me_2$), 4.86 (s, 5 H, Cp), 3.11 (s, 12 H, NMe_2), 2.32 (s, 6 H, $C_6H_3\mathit{Me}_2$); IR (cm^{-1}) 1969 (s), 1912 (s), 1236 (w), 1150 (w), 982 (w), 978 (w), 949 (s), 919 (w), 908 (w), 819 (w), 796 (m), 755 (m), 727 (m), 705 (w), 676 (m), 620 (w), 596 (w), 570 (w), 563 (m); mass spectrum, m/e 480 (M^+), 452 (−CO), 375 ($-C_6H_3Me_2$), 223 ($[Ru(CO)_2(Cp)]$). Anal. Calcd for $C_{19}H_{26}N_2O_3RuTi$: C, 47.61; H, 5.47; N, 5.84. Found: C, 47.84; H, 5.74; N, 5.52.

Preparation of $[(NMe_2)(2,6\text{-}Me_2C_6H_3O)_2TiRu(CO)_2(Cp)]$ (4). Crude $[Ti(C_6H_3Me_2O)_2(NMe_2)_2]$ (2, 0.215 g, ca. 0.43 mmol) in isooctane (15 mL) was added to a solution of $[RuH(CO)_2(Cp)]$ made from $[Ru_3(CO)_{12}]$ (0.1347 g, 0.2107 mmol) and cyclopentadiene (1.5 mL) in heptane (50 mL). The clear, yellow solution was stirred ca. 15 h at room temperature, by which time it had became slightly cloudy. The reaction mixture was evaporated under vacuum to an oil, and extracted with isooctane (ca. 20 mL). The extract was then concentrated to the verge of cloudiness, and chilled at −40 °C. The mother liquor was decanted from the product, which precipitated as an orange solid, and the product was dried in vacuo: yield 0.223 g (0.400 mmol, 70.4%); mp 86–98 °C (decomp pt 54–64 °C); ^1H NMR δ 6.94 (mult, 6 H, $C_6\mathit{H}_3Me_2$), 4.80 (s, 5 H, Cp), 3.36 (s, 6 H, NMe_2), 2.30 (s, 12 H, $C_6H_3\mathit{Me}_2$); IR (cm^{-1}) 2001 (s), 1998 (s), 1951 (s), 1945 (s), 1267 (m), 1252 (s), 1239 (m), 1218 (m), 1203 (s), 1168 (w), 1098 (w), 1083 (w), 1036 (w), 1022 (w), 980 (m), 909 (w), 817 (w), 761 (m), 737 (w), 729 (w), 713 (w), 672 (w), 557 (w); mass spectrum, m/e 557 (M^+), 529 (−CO), 501 (−2CO), 334 ($[Ti(2,6\text{-}Me_2C_6H_3O)_2(NMe_2)]$), 223 ($[Ru(CO)_2(Cp)]$).

Attempted Reaction of $[RuH(CO)_2(Cp)]$ with $[Ti\{2,6\text{-}(Me_3C)_2C_6H_3O\}_2(NMe_2)_2]$. A solution of $[RuH(CO)_2(Cp)]$ made from $[Ru_3(CO)_{12}]$ (0.117 g, 0.183 mmol) and cyclopentadiene (1.0 mL) in heptane (50 mL) was stirred with $[Ti\{2,6\text{-}(Me_3C)_2C_6H_3O\}_2(NMe_2)_2]$ (0.270 g, 0.495 mmol) while the IR spectrum was monitored. After 12 h at room temperature, followed by 18 h at reflux, no change in the IR spectrum had occurred.

Crystal Structure Analysis of 4. X-ray quality crystals were obtained from isooctane at −40 °C, filtered, and briefly dried in vacuo. In the glove box, a suitable crystal of approximate dimensions 0.7 mm × 0.35 mm × 0.35 mm was lodged in a 0.3 mm glass capillary which was temporarily sealed with silicone grease, removed from the glovebox, and immediately flame sealed. All X-ray diffraction measurements were made by using an Enraf-Nonius CAD4 diffractometer. The unit cell was determined from 25 randomly selected reflections, which were recentered to obtain refined cell dimensions. Data were corrected for Lorentz and polarization effects. Fluctuation of the three intensity standards which occurred early in the data collection may have been due to slight movement of the crystal in its capillary; the fluctuation was not amenable to a normal correction by linear interpolation of the standard intensities. Corrections for extinction or absorption ($\mu = 9.27\ cm^{-1}$) were not needed.

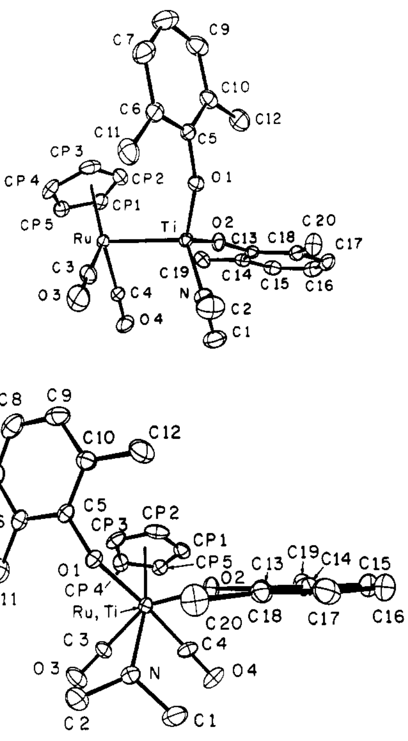


Figure 1. Two views of the structure of $[(NMe_2)(2,6\text{-}Me_2C_6H_3O)_2TiRu(CO)_2(Cp)]$ (4), plotted by using ORTEP with 50% probability ellipsoids.

Non-hydrogen atoms were located by using DIRDIF,[21] including all data with $I \geq 0$. Data with $I \geq 3\sigma(I)$ were used for the subsequent refinement of the structure by using local versions of Ibers' NUCLS least-squares program (based on the Busing–Levy ORFLS), Zalkin's FORDAP Fourier program, and Johnson's ORTEP thermal ellipsoid plotting program.[35] Non-hydrogen atoms were refined by using anisotropic thermal parameters. Anomalous dispersion corrections were included for the scattering of Ru and Ti. Least-squares refinements minimized the function $\sum_{hkl} w(F_o - F_c)^2$ where the weighting factor was $w = 1/\sigma(F_o)^2$. At least one hydrogen atom on each carbon was located by using difference Fourier methods. The remaining hydrogen atoms were placed in idealized positions with $d(C\text{–}H) = 1.0$ Å and $B = 6.0$ Å^2; their positions were adjusted after each cycle of refinement. Additional details of the crystal structure are presented in Table I.

Results

Reactions of $[Ti(NMe_2)_4]$ with $2,6\text{-}Me_2C_6H_3OH$ gave mixed aryloxy amides of titanium, $[Ti(2,6\text{-}Me_2C_6H_3O)(NMe_2)_3]$ (1) and $[Ti(2,6\text{-}Me_2C_6H_3O)_2(NMe_2)_2]$ (2), in sufficient purity for subsequent reactions. When 1 equiv of $[RuH(CO)_2(Cp)]$ reacted with 1 and 2, the products $[(NMe_2)_2(2,6\text{-}Me_2C_6H_3O)TiRu(CO)_2(Cp)]$ (3) and

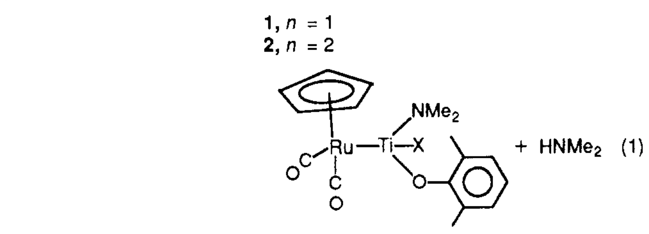
---

(21) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. J.; Gould, R. O.; van den Hark, T. E. M.; Prick, P. A.; Noorkik, J. H.; Beurskins, G.; Parthasarthi, V.; Bruinsslot, H. J.; Haltiwanger, R. C. DIRDIF; Crystallography Laboratory, Toernooiveld, Technical Report 1983/1, 1983; 6525 ED Nikmegan, Netherlands.

Table I. Summary of Crystal Data and Details of Intensity Collection and Refinement for $[(NMe_2)(2,6\text{-}OC_6H_3Me_2)_2TiRu(CO)_2(Cp)]$ (4)

Crystal Data	
formula	$C_{25}H_{29}NO_4RuTi$
fw	556.49
space group	$P2_1/n$ (No. 14)
a, Å	8.201 (3)
b, Å	18.776 (4)
c, Å	16.739 (6)
β, deg	103.90 (3)
unit cell volume, Å^3	2526.29
Z	4
$F(000)$	284
ρ_{calc}, g·cm^{-3}	1.463
Data Collection	
radiation	Mo Kα
λ, Å	0.71073
sets of setting angles refined	25
θ range, deg	0–25
temp, °C	23
max counting time, s	90
h,k,l ranges	0 to 9, 0 to 22, −19 to 19
scan type	ω–2θ
scan range	$0.65 \pm 0.35 \tan\theta$
no. of stds	3
max variatn, %	47
unique data	4683
data with $I \geq 3\sigma(I)$	2972
Structure Solution and Refinement	
p factor for calculation of $\sigma(I)$	0.02
final no. of variables	289
max shift/error in last cycle	0.15
R	5.6
R_w	6.5
error in observn of unit wt	2.40
largest peak in final diff Fourier, e/Å^3	0.12 near Ru
μ, abs coeff, cm^{-1}	9.27
absorptn correctn	none
extinctn correctn	none

$[(NMe_2)(2,6\text{-}Me_2C_6H_3O)_2TiRu(CO)_2(Cp)]$ (**4**), respectively, were formed (eq 1).



3, X = NMe_2
4, X = $2,6\text{-}Me_2C_6H_3O$

When $[FeH(CO)_2(Cp)]$ reacted with **1** or **2**, IR monitoring showed carbonyl absorptions consistent with the formation of iron analogues of **3** and **4**, and a yellow solid tentatively identified as $[(NMe_2)(2,6\text{-}Me_2C_6H_3O)_2TiFe(CO)_2(Cp)]$ (IR ν(CO) 1968, 1922 cm^{-1}; δ(Cp) 4.40) was isolated. Unfortunately, attempted recrystallization produced only $[Fe_2(CO)_4(Cp)_2]$, even at −40 °C. Attempts to react $[RuH(CO)_2(Cp)]$ with $[Ti(2,6\text{-}Me_2C_6H_3O)_3(NMe_2)]$ and $[Ti\{2,6\text{-}(Me_3C)_2C_6H_3O\}_2(NMe_2)_2]$ were not successful. In the former case, diaryloxide **2** present as an impurity was scavenged by the ruthenium hydride. In the latter case, no reaction occurred even in refluxing heptane.

Ruthenium–titanium compounds **3** and **4** are extremely air-sensitive, yellow, crystalline solids but are sufficiently robust and volatile to display molecular ions in their EI mass spectra. Proton NMR and infrared spectra are consistent with the proposed structures (Table III). The structure of **4** was determined by X-ray diffraction. Crystal data, positional and equivalent isotropic thermal parameters, bond distances, and bond angles are presented in Table I, II, IV, and V, respectively; details of the structure are discussed below.

Table II. Positional and Equivalent Isotropic Thermal Parameters[a] for the Atoms of $[(NMe_2)(2,6\text{-}OC_6H_3Me_2)_2TiRu(CO)_2(Cp)]$ (4)

atom	x	y	z	B_{eq}, Å^2
Ru	0.32088 (8)	0.27003 (3)	0.35514 (4)	3.1
Ti	0.2593 (2)	0.33857 (6)	0.21807 (8)	2.8
O1	0.2338 (6)	0.2718 (3)	0.1377 (3)	3.4
O2	0.4208 (6)	0.4018 (3)	0.2171 (3)	4.0
O3	−0.0529 (8)	0.2656 (4)	0.3238 (5)	7.4
O4	0.310 (1)	0.4119 (3)	0.4358 (4)	6.6
N	0.0649 (8)	0.3914 (3)	0.2044 (4)	4.1
C1	0.073 (1)	0.4626 (5)	0.2414 (7)	6.5
C2	−0.100 (1)	0.3720 (6)	0.1580 (7)	6.6
C3	0.091 (1)	0.2672 (5)	0.3368 (5)	4.5
C4	0.314 (1)	0.3581 (5)	0.4040 (5)	4.8
C5	0.273 (1)	0.2095 (4)	0.1054 (4)	3.3
C6	0.166 (1)	0.1514 (4)	0.1026 (5)	3.9
C7	0.210 (1)	0.0886 (5)	0.0720 (6)	5.4
C8	0.354 (2)	0.0816 (5)	0.0474 (7)	6.4
C9	0.457 (1)	0.1393 (6)	0.0490 (6)	5.5
C10	0.418 (1)	0.2047 (5)	0.0769 (5)	4.2
C11	0.010 (1)	0.1574 (5)	0.1302 (6)	5.7
C12	0.525 (1)	0.2697 (6)	0.0756 (7)	6.3
C13	0.487 (1)	0.4639 (4)	0.1957 (5)	3.3
C14	0.6164 (9)	0.4954 (4)	0.2512 (5)	3.8
C15	0.684 (1)	0.5570 (5)	0.2282 (6)	4.8
C16	0.622 (1)	0.5870 (5)	0.1519 (7)	5.7
C17	0.491 (1)	0.5550 (5)	0.0982 (6)	5.0
C18	0.420 (1)	0.4939 (4)	0.1176 (5)	3.8
C19	0.683 (1)	0.4633 (5)	0.3348 (6)	5.3
C20	0.270 (1)	0.4609 (5)	0.0585 (6)	5.5
CP1	0.591 (1)	0.2415 (5)	0.3922 (6)	4.8
CP2	0.537 (1)	0.2240 (6)	0.3111 (6)	5.5
CP3	0.421 (1)	0.1707 (5)	0.3094 (6)	5.6
CP4	0.408 (1)	0.1566 (4)	0.3909 (7)	5.3
CP5	0.517 (1)	0.2017 (5)	0.4403 (6)	4.6

[a] The equivalent displacement parameter is defined as $^4/_3$ Tr$(\beta \cdot G)$, where $\beta_{ij} = 2\pi^2 a_i^* a_j^* U_{ij}$.

Table III. Spectroscopic Data for Ruthenium–Titanium Compounds and Related Species

compound[a]	ν(CO),[b] cm^{-1}	δ(Cp)[c]
$[(NMe_2)_2(ArO)TiRu(CO)_2(Cp)]$ (**3**)	1969, 1912	4.86
$[(NMe_2)(ArO)_2TiRu(CO)_2(Cp)]$ (**4**)	2001, 1998, 1951, 1945	4.80
$[(NMe_2)_3TiRu(CO)_2(Cp)]$ (**5**)[d]	1967, 1908	4.81
$[(NMe_2)_2(Me_2CHO)TiRu(CO)_2(Cp)]$[d]	1978, 1922	4.88
$[(NMe_2)(Me_2CHO)_2TiRu(CO)_2(Cp)]$[d]	1989, 1979, 1931, 1922	4.92
$[(Me_2CHO)_3TiRu(CO)_2(Cp)]$[d]	1981, 1931	5.02
$[(Cp)_2(OCMe_3)ZrRu(CO)_2(Cp)]$[e]	1958, 1984[f]	4.61
$[Ru(GeMe_3)(CO)_2(Cp)]$[g]	2016, 1957[h]	4.99[i]
$Na[Ru(CO)_2(Cp)]$[j]	1904, 1825[k]	...

[a] Ar = $2,6\text{-}Me_2C_6H_3$. [b] Isooctane solution except as noted. [c] C_6D_6 solution except as noted. [d] Reference 16. [e] Reference 7a. [f] KBr. [g] Reference 26. [h] Hexane solution. [i] $CDCl_3$ solution. [j] Reference 8a. [k] THF solution.

Discussion

Synthesis. The mixed titanium aryloxy amides $[Ti(2,6\text{-}Me_2C_6H_3O)(NMe_2)_3]$ (**1**), $[Ti(2,6\text{-}Me_2C_6H_3O)_2(NMe_2)_2]$ (**2**), $[Ti(2,6\text{-}Me_2C_6H_3O)_3(NMe_2)]$, and $[Ti\{2,6\text{-}(Me_3C)_2C_6H_3O\}_2(NMe_2)_2]$ were prepared by amine elimination (eq 2, n = 1–3). Inseparable mixtures of mixed

$$[Ti(NMe_2)_4] + nROH \rightarrow [Ti(OR)_n(NMe_2)_{4-n}] + nMe_2NH \quad (2)$$

alkoxy amides are often produced in reactions such as (2)

Table IV. Bond Distances (Å) with Esd's for [(NMe$_2$)(C$_6$H$_3$Me$_2$O)$_2$TiRu(CO)$_2$(Cp)]

Ru–Ti	2.573 (1)	C5–C6	1.40 (1)
Ru–C3	1.858 (8)	C5–C10	1.39 (1)
Ru–C4	1.853 (9)	C6–C7	1.37 (1)
Ru–CP1	2.240 (8)	C6–C11	1.47 (1)
Ru–CP2	2.260 (8)	C7–C8	1.35 (1)
Ru–CP3	2.248 (8)	C8–C9	1.38 (1)
Ru–CP4	2.282 (8)	C9–C10	1.38 (1)
Ru–CP5	2.283 (9)	C10–C12	1.51 (1)
Ru–CP0[a]	1.938 (9)		
		C13–C14	1.37 (1)
Ti–N	1.858 (6)	C13–C18	1.41 (1)
Ti–O1	1.814 (5)	C14–C15	1.38 (1)
Ti–O2	1.791 (5)	C14–C19	1.50 (1)
		C15–C16	1.38 (1)
O1–C5	1.362 (8)	C16–C17	1.37 (1)
O2–C13	1.372 (8)	C17–C18	1.36 (1)
O3–C3	1.155 (9)	C18–C20	1.52 (1)
O4–C4	1.146 (9)		
		CP1–CP2	1.36 (1)
N–C1	1.47 (1)	CP1–CP5	1.35 (1)
N–C2	1.44 (1)	CP2–CP3	1.38 (1)
		CP3–CP4	1.42 (1)
		CP4–CP5	1.36 (1)

[a] CPO is the centroid of the cyclopentadienyl ring.

Table V. Bond Angles (deg) with Esd's for [(NMe$_2$)(C$_6$H$_3$Me$_2$O)$_2$TiRu(CO)$_2$(Cp)]

Ti–Ru–C3	83.8 (3)	O1–C5–C6	118.0 (7)
Ti–Ru–C4	85.8 (2)	O1–C5–C10	120.0 (7)
Ti–Ru–CP0	115.6 (3)	C5–C6–C7	117.0 (8)
CP0[a]–Ru–C3	134.8 (4)	C5–C6–C11	121.1 (8)
CP0[a]–Ru–C4	131.7 (4)	C6–C7–C8	122.1 (9)
C3–Ru–C4	87.6 (4)	C7–C8–C9	120.4 (9)
		C8–C9–C10	120.7 (9)
Ru–Ti–N	111.0 (2)	C9–C10–C5	117.7 (8)
Ru–Ti–O1	106.2 (2)		
Ru–Ti–O2	110.5 (2)	O2–C13–C14	119.1 (7)
N–Ti–O1	109.5 (3)	O2–C13–C18	119.3 (7)
N–Ti–O2	105.7 (3)	C13–C14–C15	118.4 (8)
O1–Ti–O2	113.9 (2)	C13–C14–C19	120.7 (7)
		C14–C15–C16	121.8 (8)
Ti–O1–C5	153.2 (5)	C15–C16–C17	119.3 (8)
Ti–O2–C13	155.7 (5)	C16–C17–C18	122.1 (9)
		C17–C18–C13	117.4 (8)
Ti–N–C1	119.0 (6)	C17–C18–C20	121.4 (8)
Ti–N–C2	127.5 (6)		
C1–N–C2	113.4 (7)	CP5–CP1–CP2	111.8 (9)
		CP1–CP2–CP3	105.0 (8)
Ru–C3–O3	178.7 (8)	CP2–CP3–CP4	109.0 (8)
Ru–C4–O4	178.5 (8)	CP3–CP4–CP5	105.9 (8)
		CP4–CP5–CP1	108.2 (9)

[a] CP0 is the centroid of the cyclopentadienyl ring.

because of facile dismutation and redistribution reactions,[22] as we observed in our preparations of bis(aryloxide) **2** and tris(aryloxide) [Ti(2,6-Me$_2$C$_6$H$_3$O)$_3$(NMe$_2$)], each of which contained 20–25% of the other compound according to ^{1}H NMR spectra. Reactions of [Ti(NMe$_2$)$_4$] with less than 4 equiv of phenol, 4-cresol, 2,2,2-trifluoroethanol, and *tert*-butyl alcohol also gave inseparable product mixtures that hindered further investigations of these systems.

Reactions of 1 equiv of [RuH(CO)$_2$(Cp)] with either **1** or **2** to give [(NMe$_2$)$_2$(2,6-Me$_2$C$_6$H$_3$O)TiRu(CO)$_2$(Cp)] (**3**) and [(NMe$_2$)(2,6-Me$_2$C$_6$H$_3$O)$_2$TiRu(CO)$_2$(Cp)] (**4**), respectively, are similar to our earlier report of amine eliminations forming ruthenium–titanium compounds with dimethylamide and isopropoxide ligands of titanium.[16] However, in contrast with the reaction of two [RuH(CO)$_2$(Cp)] with [Ti(OCHMe$_2$)$_2$(NMe$_2$)$_2$] to give [(OCHMe$_2$)$_2$Ti{Ru(CO)$_2$(Cp)}$_2$], attempts to eliminate a second amine from either **3** or **4** using an excess of [RuH(CO)$_2$(Cp)] were not successful. The presence of tris(aryloxide) [Ti(2,6-Me$_2$C$_6$H$_3$O)$_3$(NMe$_2$)] in our sample of bis(aryloxide) **2** did not adversely affect the preparation of **3**, because [RuH(CO)$_2$(Cp)] does not react with the tris(aryloxide). Similarly, no reaction occurs between [RuH(CO)$_2$(Cp)] and [Ti{2,6-(Me$_3$C)$_2$C$_6$H$_3$O}$_2$(NMe$_2$)$_2$]. We attribute these failures to steric crowding, which shields the titanium amide groups from the ruthenium hydride.

Spectroscopic Characterization. Amide ligands are good π- and σ-donors.[23,24] Alkoxides are weaker donors in both respects, and aryloxides are weaker still.[25] These differences are reflected in the spectroscopic properties of Ru–Ti compounds **3** and **4** (Table III). The carbonyl stretching frequencies of complexes **3** and **4** are much higher than those of the [Ru(CO)$_2$(Cp)]$^-$ anion[7,8] and almost as high as analogous group 14 compounds such as [Ru(GeMe$_3$)(CO)$_2$(Cp)],[26] suggesting that the Ru–Ti bonds have predominantly covalent character with little Ti$^+$–Ru$^-$ polarization. Relative to [(NMe$_2$)$_3$TiRu(CO)$_2$(Cp)] (**5**) and the mixed isopropoxide complexes, the carbonyl stretching frequencies of **3** and **4** move to higher wavenumbers, showing a *decrease* in electron density at ruthenium due to changes in the titanium environment (vide infra). Compound **4** shows splitting of its infrared stretches into four bands, as was also observed for bis(isopropoxide) [(NMe$_2$)(Me$_2$HCO)$_2$TiRu(CO)$_2$(Cp)], perhaps reflecting the presence of rotational isomers which interchange slowly on the infrared time scale.

On the basis of the gradual downfield shift of the ruthenium cyclopentadienyl resonances in ^{1}H NMR spectra as dimethylamide ligands are replaced by isopropoxides (Table III)[16] and the observed infrared trend, one would expect the Cp resonances of **3** and **4** to shift progressively to even lower field. Surprisingly, the Cp shift of bis(aryloxide) complex **4** is about equal to that of [(NMe$_2$)$_3$TiRu(CO)$_2$(Cp)]. Rather than attributing this to an unexpected increase in electron density at ruthenium in **4**,[27] we believe that the ring currents of the aryloxide groups in the relatively crowded environment of **4** cause this anomalous shift to higher field. We previously reported an anomalous *downfield* shift in the Cp resonance of [Fe{HC(PPh$_2$)$_3$}(Cp)][PF$_6$], attributed to the ring currents of six phenyl groups oriented *perpendicular* to the Cp ring.[28]

Molecular Structure of [(NMe$_2$)(2,6-Me$_2$C$_6$H$_3$O)$_2$TiRu(CO)$_2$(Cp)] (4). The most important structural feature of [(NMe$_2$(2,6-Me$_2$C$_6$H$_3$O)$_2$TiRu(CO)2(Cp)] (**4**) is the ruthenium–titanium bond length of 2.573 (1) Å. There are no bridging ligands, and in particular there is no σ- or π-interaction of the carbonyl ligands with titanium. The distances from titanium to C3, O3, C4, and

---

(22) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1985**, *24*, 3058–3062.

(23) (a) Lappert, M. F.; Power, P. D.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Ellis Harwood Ltd.: Chichester, 1980. (b) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Eds.; Pergamon: Oxford, England, 1987; Vol. 2, Chapter 13.4. (c) Andersen, R. A.; Beach, D. B.; Jolly, W. L. *Inorg. Chem.* **1985**, *24*, 4741.

(24) (a) Buhro, W. E.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 905–906. (b) Bradley, D. C.; Newing, C. W.; Chisholm, M. H.; Kelly, R. L.; Haitko, D. A.; Little, D.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1980**, *19*, 3010.

(25) (a) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G.; Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, England, 1987; Vol. 2, Chapter 15.3. (b) Coffindaffer, T. W.; Rothwell, I. P.; Huffmann, J. C. *Inorg. Chem.* **1983**, *22*, 2906–2910. (c) Coffindaffer, T. W.; Rothwell, I. P.; Huffmann, J. C. *Inorg. Chem.* **1984**, *23*, 1433–1436.

(26) Sosinsky, B. A.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1633–1640.

(27) Treichel, P. M.; Komar, D. A. *Synth. React. Inorg. Met.-Org. Chem.* **1980**, *10*, 205.

(28) Goodrich, J. D.; Selegue, J. P. *Organometallics* **1985**, *4*, 798.

O4 are 3.005 (6), 3.727 (6), 3.058 (6), and 3.824 (6) Å, respectivley, all well outside the range for bonds to titanium. Shriver's Ω parameter,[29] which is typically 2.0–2.5 for conventional C-bridging CO, 2.5–3.0 for Π-CO, and 4.5–5.0 for Σ-CO, is 2.24 and 2.23 for carbonyls C3–O3 and C4–O4, respectively.

The titanium atom is tetrahedrally coordinated by two 2,6-$Me_2C_6H_3O$ groups, one NMe_2 group, and the [Ru($CO)_2$(Cp)] group. The NMe_2 ligand is planar, with a short Ti–N bond reflecting the strong π-donor ability of this ligand.[23] The NMe_2 group is rotated such that one dimethylamido methyl carbon is proximal to ruthenium (*d*(Ru–C1) = 4.363 (6) Å) and the other is distal (*d*(Ru–C2) = 4.600(6) Å). The Ti–N–C(distal) angle is 6.5° more obtuse than the Ti–N–C(proximal) angle, slightly less than the ca. 10° differences found in [$(NMe_2)_3TiRu(CO)_2$(Cp)] (**5**) and [$(NMe_2)_3TiFe(CO)_2$(Cp)].[16,17] This proximal/distal distortion of amide ligands has been observed for other electron-deficient metal amides and is especially pronounced for amide compounds with metal–metal multiple bonds.[17,24] The geometry of the aryloxide oxygen atoms is nearly linear (average 154.4°). Aryloxide ligands often display this structural feature, which minimizes steric repulsions while maximizing π-overlap of the oxygen orbitals with both the metal and the aryl group.[25] The [Ru$(CO)_2$(Cp)] moiety is structurally very similar to that in [$(NMe_2)_3TiRu(CO)_2$(Cp)] (**5**)[16] and related mixed-metal compounds.[7,8] Substituents on the two metals are roughly staggered, with torsion angles C3–Ru–Ti–N, C4–Ru–Ti–N, and CP0–Ru–Ti–O1 of 31.6°, 56.5°, and 49.8°, respectively, compared to 60° for an ideally staggered structure.

Compound **4** is sterically crowded. The nonbonding distances between the following atoms are equal to or shorter than the sums of appropriate van der Waals radii[30] (in parentheses): C5–CP3, 3.417 (6) Å (3.40 Å); C3–CP4, 3.302 (6) Å (3.40 Å); N–C3, 3.190 (6) Å (3.25 Å); and C1–O2, 3.214 (6) Å (3.50 Å). These close, nonbonding approaches suggest that the staggered orientation of substituents on titanium and ruthenium is sterically determined. There are no unusually close intermolecular contacts.

The 2.573 (1) Å ruthenium–titanium bond in **4** is 0.090 Å shorter than the 2.663 (1) Å bond in [$(NMe_2)_3$TiRu$(CO)_2$(Cp)] (**5**), the only previously reported ruthenium–titanium bond.[16] While a single example of a bond attenuation of less than 0.1 Å must be approached with caution, we feel that the difference is significant. Sterically, the *local* crowding about titanium is slightly decreased in **4** compared to tris(amide) **5**, as the oxygen atoms of the aryloxides bear only one substituent instead of two. However, this effect is overshadowed by the greater *overall* crowding in the molecule caused by the bulky xyloxy groups. The close intermolecular contacts would tend to lengthen the metal–metal bond, contrary to what is observed.

The shorter ruthenium–titanium bond in **4** compared to **5** must then be ascribed to electronic effects. Similar effects have been examined in detail for analogous iron–group 14 compounds [Fe$(EX_3)(CO)_2$(Cp)] (E = Si, Ge, Sn).[31] In particular, the iron–tin bonds in [Fe(SnX_3)-$(CO)_2$(Cp)] are invariably shorter than "expected" lengths derived by summing covalent radii and are sensitive to the substituents on tin, ranging from 2.462 (2) Å for [Fe$(SnBr_3)(CO)_2$(Cp)][32] to 2.601 (5) and 2.603 (5) Å for [{Fe$(CO)_2$(Cp)}$_2$(μ-$SnMe_2$)].[33] Transition-metal d_π to group 14 element d_π electron donation had been suggested to account for this shortening, but spectroscopic studies failed to support this idea. Both structural and spectroscopic studies suggest that transition metal–group 14 bonds are almost purely σ in character. Varying amounts of s character in the sp^x–hybridized group 14 element, influenced by the electronegativities of the tin substituents, satisfactorily account for the observed shortening. A similar σ-based explanation could explain the shorter metal–metal bond in **4**, since aryloxides are less electronegative than amides. However, the group 4 metals are more electropositive than group 14, and their d orbitals are much more involved in bonding. Therefore, we suggest that the shorter ruthenium–titanium bond in **4** may be *partially* due to more effective electron donation from ruthenium d_π to titanium d_π orbitals, promoted by the relative electron deficiency at titanium in **4**. To the contrary, Xα–SW molecular orbital calculations on [$(Cp)_2$IMRu$(CO)_2$(Cp)] (M = Zr, Th) suggest that the metal–metal bond is best described as σ-donation from ruthenium $4d_{z^2}/4d_{xz}$ orbitals to zirconium 4d or thorium 6d/5f orbitals, with little π-donation.[34] In that study, Bursten suggested that heterobimetallics with "more covalent" metal–metal bonds may exhibit very different properties. Perhaps the ruthenium–titanium compounds discussed here, with very electron-deficient titanium centers lacking cyclopentadienyl ligands, fit this description. A molecular orbital study of their bonding would be instructive.

Conclusion. Amine elimination reactions between early-transition-metal amides and late-transition-metal hydrides provide a route to heterobimetallics with a variety of substituents on the early metal. Steric crowding at the early metal may prevent amine elimination from occurring. Changes in the ligand environment of titanium clearly induce secondary changes in the ruthenium–titanium bond length and the spectroscopic properties of the [Ru$(CO)_2$-(Cp)] group.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, Occidental Research Corp., the Institute for Mining and Minerals Research (subgrant from the U.S. Bureau of Mines), and Ashland Oil Corp. for financial support of this research; the Alexander von Humboldt Foundation for sabbatical support to J.P.S.; and Engelhard Industries, Johnson Matthey, Inc., and Colonial Metals for generous loans of ruthenium trichloride.

Registry No. **1**, 121730-47-0; **2**, 109306-88-9; **3**, 121730-50-5; **4**, 121730-51-6; 2,6-$Me_2C_6H_3OH$, 576-26-1; [Ti$(NMe_2)_4$], 3275-24-9; [Ti(2,6-$Me_2C_6H_3O)_3(NMe_2)$], 121730-48-1; [Ti{2,6-$(CMe_3)_2C_6H_3O$}$_2(NMe_2)_2$], 121730-49-2; 2,6-$(CMe_3)_2C_6H_3OH$, 128-39-2; [RuH$(CO)_2$(Cp)], 57349-59-4; Ru, 7440-18-8; Ti, 7440-32-6.

Supplementary Material Available: Tables of anisotropic thermal parameters, parameters for fixed hydrogen atoms, and least-squares planes for **4** (4 pages); a listing of observed and calculated structure factors for **4** (19 pages). Ordering information is given on any current masthead page.

---

(29) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219.

(30) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1973; p 260.

(31) (a) Mackay, K. M.; Nicholson, B. K. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 6, Chapter 43. (b) Greene, P. T.; Bryan, R. F. *J. Chem. Soc. A* **1970**, 2261–2266.

(32) Melson, G. A.; Stokeley, P. F.; Bryan, R. F. *J. Chem. Soc. A* **1970**, 2247.

(33) (a) Biryukov, B. P.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1968**, *9*, 488. (b) Biryukov, B. P.; Struchkov, Yu, T.; Anisimov, K. N.; Kolobova, N. E.; Skripkin, V. V. *Chem. Commun.* **1968**, *159*–160.

(34) Bursten, B. E.; Novo-Gradac, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 904–905.

(35) Johnson, C. K. Report ORNL 5138, 1976; Oak Ridge National Laboratory, Oak Ridge, TN.