lecular interactions. A related coordination environment for lithium has been observed in $LiAl(N{=}C\text{-}t\text{-}Bu_2)_4$[23] and in complexes containing very bulky alkoxides.[24]

The use of bulky nitrogen-based ligands has allowed the isolation of thermally stable four-coordinate alkyl complexes, which, in preliminary experiments, do not show reactivity toward olefins. Efforts are in progress to synthesize more reactive alkylvanadium complexes, a long-term goal being the formation of coordinatively and electronically unsaturated three-coordinate species.

Registry No. **1**, 127971-45-3; **2**, 127971-46-4; **3a**, 127971-47-5; **3b**, 127971-48-6; **3c**, 127971-43-1; **4**, 127971-44-2; $VOCl_3$, 7727-18-6; $t\text{-}Bu_3SiNHLi$, 82135-42-0.

Supplementary Material Available: Full details of the preparation and characterization of the compounds, details of the structure determination of 4, and tables of the atomic coordinates, bond distances and angles, anisotropic displacement parameters, and hydrogen atomic parameters (11 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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[23] Rhine, W. E.; Stucky, G.; Peterson, S. W. *J. Am. Chem. Soc.* **1975**, *97*, 6401.

[24] (a) Murray, B. D.; Power, P. P. *J. Am. Chem. Soc.* **1984**, *106*, 7011. (b) Stewart, J. L.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 1846.

Selective Synthesis of Functionalized Alkylidynetriosmium Compounds via Silicon and Tin Reagents

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Received April 18, 1990

Summary: Selective transformation of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ (**1**) to a variety of the functionalized triosmium alkylidyne cluster compounds $H_3Os_3(CO)_9(\mu_3\text{-}CR)$ (R = $CH_2CH{=}CH_2$ (**2**), H (**3**), CH_3 (**4**), Ph (**5**), $p\text{-}C_6H_4CH_3$ (**6a**), $CH_2C(O)Bu^t$ (**7**)) is achieved by the treatment of **1** with $AgSbF_6$ in the presence of silicon and tin nucleophiles. Acyl functional groups (R = C(O)OMe (**9**), $C(O)CH_2CH{=}CH_2$ (**10**), $C(O)CH_2C(O)Bu^t$ (**11**)) are also introduced by the reaction of **1** with $AgSbF_6$ under a CO atmosphere followed by the treatment with nucleophiles.

In comparison with the classic organometallic cluster chemistry of alkylidynetricobalt compounds, $Co_3(CO)_9(\mu_3\text{-}CR)$,[1] the derivative chemistry of isoelectronic iron triad alkylidyne clusters, $H_3M_3(CO)_9(\mu_3\text{-}CR)$ (M = Fe, Ru, Os),[2,3] has been much less developed. For example, the previously known purely hydrocarbyl triosmium derivatives are limited to R = H,[4,5] CH_3,[6] CH_2CH_3,[5] CH_2Ph,[7] and Ph,[8] and the procedures used are not easily generalized. However, the promoting action of Lewis acids on the formation of the halides[8-10] and the introduction of the phenyl group[8] suggest that these reactions proceed via a carbocationic intermediate. These observations prompted us to examine reactions with nucleophilic silicon and tin reagents expected to capture such a transient species.[11]

Table I. Transformation of $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ (1) to $H_3Os_3(CO)_9(\mu_3\text{-}CR)$

entry no.	Nu	conditions	R (product)	yield, %
1	$CH_2{=}CHCH_2\text{-}SiMe_3$	reflux, 6 h	$CH_2CH{=}CH_2$ (**2**)	96
2	$HSiEt_3$	room temp, 5 min	H (**3**)	99
3	Me_4Sn	room temp, 5 min	CH_3 (**4**)	85
4	Et_4Sn	room temp, 5 min	H (**3**)	69
5	C_6H_6	reflux, 3 h	Ph (**5**)	97
6	Ph_4Sn	reflux, 2 h	Ph (**5**)	56
7	$CH_3C_6H_5$	reflux, 3 h	$C_6H_4CH_3$ (**6a** + **6b**)[a]	83
8	$(p\text{-}CH_3C_6H_4)_4Sn$	reflux, 2 h	$p\text{-}C_6H_4CH_3$ (**6a**)	51
9	$CH_2{=}C(Bu^t)\text{-}OSiMe_3$	room temp, 12 h	$CH_2C(O)Bu^t$ (**7**)	55
10	(1) CO + (2) MeOH	room temp, 10 min[b]	C(O)OMe (**9**)	45
11	(1) CO + (2) $CH_2{=}CHCH_2\text{-}SiMe_3$	reflux, 1 h[b]	$C(O)CH_2CH{=}CH_2$ (**10**)	25
12	(1) CO + (2) $CH_2{=}C(Bu^t)\text{-}OSiMe_3$	reflux, 3 h[b]	$C(O)CH_2C(O)Bu^t$ (**11**)[c]	34
13	(1) CO + (2) $HSiEt_3$	reflux, 6 h[b]	CH_3 (**4**)	61

[a] **6a**:**6b** = 2.2:1. [b] Conditions for step 2. [c] A 10:1 mixture of the enol and keto tautomers (see text).

When $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ (**1**)[9] was treated with excess $AgSbF_6$ in refluxing CH_2Cl_2 in the presence of allyltrimethylsilane, the anticipated product $H_3Os_3(CO)_9(\mu_3\text{-}CCH_2CH{=}CH_2)$ (**2**)[12] was obtained in almost quantitative yield (eq 1). Analogous reactions led to other new prod-

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[1] Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97.

[2] Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

[3] Keister, J. B. *Polyhedron* **1988**, *7*, 847.

[4] Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.

[5] Azam, K. A.; Deeming, A. J.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1981**, 91.

[6] Deeming, A. J.; Underhill, M. *J. Chem. Soc., Chem. Commun.* **1973**, 277.

[7] Chi, Y.; Chen, B.-F.; Wang, S.-L.; Chiang, R.-K.; Hwang, L.-S. *J. Organomet. Chem.* **1989**, *377*, C59.

[8] Shore, S. G.; Jan, D.-Y.; Hsu, W.-L.; Hsu, L.-Y.; Kennedy, S.; Huffman, J. C.; Wang, T.-C. L.; Marshall, A. G. *J. Chem. Soc., Chem. Commun.* **1984**, 392.

[9] Keister, J. B.; Horling, T. L. *Inorg. Chem.* **1980**, *19*, 2304.

[10] Kneuper, H.-J.; Strickland, D. S.; Shapley, J. R. *Inorg. Chem.* **1988**, *27*, 1110.

[11] The application of a similar methodology to the generalized functionalization of bridgehead organic halides has been summarized recently: Kraus, G. A.; Hon, Y.-S.; Thomas, P. J.; Laramay, S.; Liras, S.; Hanson, J. *Chem. Rev.* **1989**, *89*, 1591.

[12] A typical procedure is as follows. A CH_2Cl_2 solution (4 mL) of $AgSbF_6$ (274 mg, 0.80 mmol) was added to a mixture of **1** (70.0 mg, 0.0762 mmol) and $CH_2{=}CHCH_2SiMe_3$ (0.5 mL) dissolved in 2 mL of CH_2Cl_2, and the mixture was refluxed for 6 h. After the consumption of **1** was checked by TLC, the volatiles were removed under reduced pressure. Extraction with ether, filtration through silica gel, and preparative TLC separation (silica gel; CH_2Cl_2/hexane, 1:3) gave **2** (64.5 mg, 0.0735 mmol; 96%). The amounts of $AgSbF_6$ and allylsilane were not optimized. **2**: ^1H NMR ($CDCl_3$) δ 6.24 (1 H, ddt, J = 17.7, 9.8, 7.4 Hz, $=CH-$), 5.21 (1 H, dd, J = 17.7, 2.0 Hz, $=CH_2$, trans), 5.05 (1 H, dd, J = 9.8, 2.0 Hz, $=CH_2$, cis), 4.82 (2 H, d, J = 7.4 Hz, CH_2), −18.86 (3 H, s, Os—H); IR (C_6H_{12}) 2077 (vs), 2018 (vs), 2006 (m) cm^{-1}. Anal. Calcd for $C_{13}H_8O_9Os_3$: C, 17.77; H, 0.92. Found: C, 17.91; H, 0.85.

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$$\underset{\mathbf{1}}{H_3Os_3(CO)_9(\mu_3\text{-}CBr)} \xrightarrow[\text{Si-Nu (Sn-Nu)}]{AgSbF_6/CH_2Cl_2} \underset{\mathbf{2,\ 6a,\ 7}}{H_3Os_3(CO)_9(\mu_3\text{-}CR)} \quad (1)$$

$$R = CH_2CH{=}CH_2\ (\mathbf{2}),\ p\text{-}C_6H_4CH_3\ (\mathbf{6a}),\ CH_2C(O)Bu^t\ (\mathbf{7})$$

ucts with R = p-$C_6H_4CH_3$ (**6a**) and $CH_2C(O)Bu^t$ (**7**) (see eq 1). The identity of each product was readily confirmed by its ^1H NMR spectrum, a single hydride signal in addition to resonances appropriate for the R group; the characteristic, simple IR $\nu(C{\equiv}O)$ pattern also indicated the 3-fold symmetric structure.[13]

The results of these and other reactions conducted are summarized in Table I, which serves to illustrate the possible scope and some limitations of this methodology. Thus, reduction and methylation leading to **3** and **4** were achieved by reaction with $HSiEt_3$ and Me_4Sn, respectively, in good yields. However, attempted ethylation with Et_4Sn resulted in the formation of **3** instead. The reaction with benzene gave the parent benzylidyne complex **5** in nearly quantitative yield. On the other hand, the reaction with toluene gave a 2.2:1 mixture of the two isomers **6a** and **6b**. This regioselectivity problem was overcome by using aryltin reagents. Thus, tetraphenyltin gave **5** as well, but the reaction with tetra-p-tolyltin produced exclusively the para isomer **6a**.[14] The minor isomer **6b** is assigned as the meta derivative: apparently steric as well as electronic effects direct this Friedel–Crafts reaction. The prospects for even more general derivatives are indicated by the reaction with the silyl enol ether of pinacolone, which produced **7** after workup.[15]

Subsequent transformation of certain derivatives is also likely, as shown by the observation that catalytic hydrogenation of **2** readily afforded the butylidyne complex **8** (eq 2).[16]

$$\mathbf{2} \xrightarrow[\text{MeOH}]{H_2/Pd\text{-}C\ (5\%)} \underset{\mathbf{8}\ (81\%)}{H_3Os_3(CO)_9(\mu_3\text{-}CCH_2CH_2CH_3)} \quad (2)$$

We anticipated that in the presence of CO the reaction of **1** with $AgSbF_6$ should form the species $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)]^+$ (previously obtained by protonation of $H_2Os_3(CO)_9(\mu_3\text{-}CCO)$[17]), which would then provide a route to acyl derivatives (eq 3 and Table I). Indeed, quenching

$$\underset{\mathbf{1}}{H_3Os_3(CO)_9(\mu_3\text{-}CBr)} \xrightarrow[\text{(2) nucleophile}]{\text{(1) }Ag^+/CO/CH_2Cl_2} \underset{\mathbf{9\text{-}11}}{H_3Os_3(CO)_9(\mu_3\text{-}CC(O)R)} \quad (3)$$

$$R = OMe\ (\mathbf{9}),\ CH_2CH{=}CH_2\ (\mathbf{10}),\ CH_2C(O)Bu^t\ (\mathbf{11})$$

with methanol provided the methyl ester with R = C(O)OMe (**9**) in moderate yield, and when the atmosphere used was highly enriched ^{13}CO, only $H_3Os_3(CO)_9(\mu_3\text{-}C^{13}C(O)OMe)$ was obtained.[18] Allyltrimethylsilane and the silyl enol ether of pinacolone afforded the allyl ketone compound **10** and the 1,3-diketone compound **11**, respectively, in modest yields.[19] In chloroform **11** appeared to be a 10:1 mixture of the enol and keto tautomers, since the major isomer showed two singlet ^1H NMR absorptions at δ 16.40 and 6.14 in a 1:1 ratio and a very broad $\nu(C{=}O)$ absorption near 1600 cm^{-1}, which are characteristic of the enol form of a 1,3-diketone.[20] No acyl intermediate could be detected during the reaction with $HSiEt_3$, and only fully reduced **4** was isolated. Finally, tin reagents were generally ineffective. IR evidence[21] of a low-yield product was obtained in the case of $(CH_2{=}CH)_4Sn$, but with Me_4Sn and Ph_4Sn only the hydrolyzed product $H_3Os_3(CO)_9(\mu_3\text{-}CC(O)OH)$[22] was isolated after workup.

This new methodology allows the preparation of regioselectively labeled compounds not previously possible. When the appropriate combination of **1**, CO, $HSiEt_3$, and their isotopomers was chosen, several versions of the labeled ethylidyne complex **4** were obtained (eqs 4–6).

$$\mathbf{1}\text{-}d_3{}^{23} \xrightarrow{Ag^+/Me_4Sn} D_3Os_3(CO)_9(\mu_3\text{-}CCH_3) \quad (4)$$

$$\mathbf{1} \xrightarrow[\text{(2) }DSiEt_3]{\text{(1) }Ag^+/CO} H_3Os_3(CO)_9(\mu_3\text{-}CCD_3) \quad (5)$$

$$\mathbf{1} \xrightarrow[\text{(2) }HSiEt_3]{\text{(1) }Ag^+/^{13}CO} H_3Os_3(CO)_9(\mu_3\text{-}C^{13}CH_3) \quad (6)$$

The results described here are readily interpreted in terms of the carbocationic species $[H_3Os_3(CO)_9(\mu_3\text{-}C)]^+$, generated by bromide abstraction from **1** with Ag^+,[24] as well as the product of subsequent CO trapping, $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)]^+$. However, several ancillary observations concerning possible reaction intermediates are as follows. (1) **1** was completely consumed by $AgSbF_6$ at -78 °C; immediate (30-s) quenching with allylsilane provided only a small amount of **2** (12%) along with **3** (18%). However, the interaction of Ag^+ with **1** is apparently masked by the formation of π-complexes in the presence of silicon and

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[13] The replacement of Br in **1** by a hydrocarbyl group results in a shift of $\nu(C{\equiv}O)$ absorptions to lower frequencies by ca. 10 cm^{-1}. **1**: IR (C_6H_{12}) 2087 (vs), 2027 (vs), 2015 (m) cm^{-1}.

[14] **6a**: ^1H NMR (CD_2Cl_2) δ 7.57 (2 H, d, J = 8.2 Hz, C_6H_4), 7.04 (2 H, d, J = 8.2 Hz, C_6H_4), 2.35 (3 H, s, CH_3), -18.58 (3 H, s, Os–H); IR (C_6H_{12}) 2080 (vs), 2021 (vs), 2017 (sh), 2007 (sh) cm^{-1}. Anal. Calcd for $C_{17}H_{10}O_9Os_3$: C, 21.98; H, 1.09. Found: C, 21.63; H, 1.00. **6b**: ^1H NMR (CD_2Cl_2) δ 7.53 (1 H, s, C_6H_4), 7.47 (1 H, d, J = 7.8 Hz, C_6H_4), 7.11 (1 H, t, J = 7.6 Hz, C_6H_4), 6.88 (1 H, d, J = 7.4 Hz, C_6H_4), 2.35 (3 H, s, CH_3), -18.59 (3 H, s, Os–H).

[15] **7**: ^1H NMR ($CDCl_3$) δ 5.19 (2 H, s, CH_2), 1.23 (9 H, s, Bu^t), -18.84 (3 H, s, Os—H); IR (C_6H_{12}) 2079 (vs), 2024 (sh), 2016 (vs), 2003 (m), 1715 (w) cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_{10}Os_3$: C, 20.51; H, 1.51. Found: C, 20.58; H, 1.53.

[16] **8**: ^1H NMR ($CDCl_3$) δ 4.21–4.13 (2 H, m, CCH_2), 1.90–1.79 (2 H, m, CH_2CH_3), 1.12 (3 H, t, J = 6.9 Hz, CH_3), -18.81 (3 H, s, Os—H); IR (C_6H_{12}) 2076 (vs), 2017 (vs), 2005 (m) cm^{-1}. Anal. Calcd for $C_{13}H_{10}O_9Os_3$: C, 17.73; H, 1.14. Found: C, 17.82; H, 1.03.

[17] Sievert, A. C.; Strickland, D. S.; Shapley, J. R.; Steinmetz, G. R.; Geoffroy, G. L. *Organometallics* **1982**, *1*, 214.

[18] ^1H NMR ($CDCl_3$): δ 3.82 (3 H, d, $^3J(^{13}C\text{–}H)$ = 4.1 Hz, OCH_3), -19.40 (3 H, s, Os—H). ^{13}C NMR ($CDCl_3$): δ 187.1 ($COOCH_3$).

[19] **10**: ^1H NMR ($CDCl_3$) δ 6.18 (1 H, ddt, J = 15.9, 10.4, 6.9 Hz, =CH–), 5.20 (1 H, dd, J = 15.9, 1.4 Hz, $=CH_2$, trans), 5.19 (1 H, dd, J = 10.4, 1.4 Hz, $=CH_2$, cis), 3.71 (2 H, dt, J = 6.9, 2.0 Hz, CH_2), -19.31 (3 H, s, Os—H); IR (C_6H_{12}) 2088 (vs), 2027 (vs), 2023 (vs), 1645 (w), 1631 (vw) cm^{-1}. Anal. Calcd for $C_{14}H_8O_{10}Os_3$: C, 18.54; H, 0.89. Found: C, 18.66; H, 0.86. **11**: ^1H NMR ($CDCl_3$, enol) δ 16.40 (1 H, s, OH), 6.14 (1 H, s, CH), 1.19 (9 H, s, Bu^t), -19.23 (3 H, s, Os—H); ^1H NMR ($CDCl_3$, keto) 4.14 (2 H, s, CH_2), 1.20 (9 H, s, Bu^t), -19.33 (3 H, s, Os—H); IR (C_6H_{12}) 2087 (vs), 2025 (vs), 1591 (w, vbr) cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_{11}Os_3$: C, 21.16; H, 1.46. Found: C, 21.27; H, 1.61. A typical procedure is as follows. CO was bubbled through a CH_2Cl_2 solution (10 mL) of **1** (49.8 mg, 0.0543 mmol) for 15 min. Then $AgSbF_6$ (93 mg, 0.27 mmol) in 2 mL of CH_2Cl_2 was added, and the mixture was stirred for 15 min at room temperature. During that time the solution changed from colorless to yellow and finally to dark brown. Then $CH_2{=}C(Bu^t)OSiMe_3$ (0.15 mL) was added via a syringe, and the mixture was refluxed for 3 h. Evaporation of the volatiles, filtration through silica gel with CH_2Cl_2, and preparative TLC separation (silica gel; CH_2Cl_2/hexane, 1.5:1) gave **11** (17.6 mg, 0.0182 mmol; 34%).

[20] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981.

[21] Compounds with an acyl functional group contain $\nu(C{\equiv}O)$ bands at almost the same positions as those of **1**. Additional characteristic features are $\nu(C{=}O)$ and hydride ^1H NMR signals appearing at higher field than δ -19.

[22] Krause, J.; Jan, D.-Y.; Shore, S. G. *J. Am. Chem. Soc.* **1987**, *109*, 4416.

[23] Yeh, W.-Y.; Kneuper, H.-J.; Shapley, J. R. *Polyhedron* **1988**, *7*, 961.

[24] Attempted abstraction of X^- from $H_3Os_3(CO)_9(\mu_3\text{-}CX)$ (X = Br, OMe) with $AlCl_3$ (Br), $TlPF_6$ (Br), $TiCl_4$ (OMe), and trimethylsilyl triflate (OMe) in the presence of allylsilane resulted in formation of a complicated mixture of products (Al) or recovery of the starting complexes (Tl, Ti, and Si).

tin reagents with unsaturated organic moieties, and heating the CH_2Cl_2 solution under reflux is necessary. In attempted vinylation by $(CH_2{=}CH)_4Sn$ and alkynylation by $HC{\equiv}CSiMe_3$ 1 was recovered quantitatively, apparently due to irreversible formation of the π-complexes. (2) It is noteworthy that silver metal deposited upon mixing $HSiEt_3$ or R_4Sn with $AgSbF_6$, whether 1 was present or not. Furthermore, in model experiments with $Ph_3CBr/AgSbF_6$ or $[Ph_3C]PF_6$ in place of $1/AgSbF_6$, Ph_3CH was obtained with $HSiEt_3$ and Et_4Sn, but Ph_3CMe was not formed with Me_4Sn. These results suggest that some Ag–Me species may alkylate 1 to give 4.[25] (3) The role of exogenous carbon monoxide in the formation of acyl derivatives, e.g. 9,[18] contrasts with the intramolecular CO migration involved in forming the tricobalt species $[Co_3(CO)_9(CCO)]^+$, which also is apparently more electrophilic in further reactions to form $Co_3(CO)_9(\mu_3\text{-}CC(O)R)$ compounds.[1] However, similar trapping of external CO by mononuclear $[CpFe(CO)_2(CH_2)]^+$ and dinuclear $[Cp_2Fe_2(CO)_3(\mu\text{-}CH)]^+$ has been observed, affording the ketene complex $[CpFe(CO)_2(CH_2{=}C{=}O)]^+$ [26] and the ketenyl complex $[Cp_2Fe_2(CO)_3(\mu\text{-}CH{=}C{=}O)]^+$,[27] respectively. Work aimed at the direct observation of intermediates in the triosmium reactions is underway.

Acknowledgment. We are grateful to D. S. Strickland for her preliminary work with $[H_3Os_3(CO)_9(CCO)]^+$ and $HSiEt_3$. This research was supported by National Science Foundation Grant CHE 89-15349.

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(25) Methylation by $AlMe_3$ and $LiCuMe_2$, which was reported to be effective in the alkylation of bridgehead organic halides, was unsuccessful: (a) Gorlier, J.-P.; Hamon, L.; Levisalles, J.; Wagnon, J. *J. Chem. Soc., Chem. Commun.* **1973**, 88. (b) Della, E. W.; Bradshaw, T. K. *J. Org. Chem.* **1975**, *40*, 1638. (c) Kraus, G. A.; Yi, P. *Synth. Commun.* **1988**, *18*, 473.

(26) Bodnar, T. W.; Cutler, A. R. *J. Am. Chem. Soc.* **1983**, *105*, 5926.

(27) Casey, C. P.; Fagan, P. J.; Miles, W. H.; Marder, S. R. *J. Mol. Catal.* **1983**, *21*, 173.

Formation, Fragmentation, and Isomerization of Titanacycle Rings Supported by Aryloxide Ligation

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Received May 18, 1990

Summary: The reactivity of the titanacyclopentadiene ring in $[(Ar''O)_2Ti(C_4Et_4)]$ can best be explained on the basis of facile fragmentation into a titanium bis(alkyne) complex.

The last few years have seen an intense research interest into the structure and reactivity of metallacycle- and heterometallacycle-containing compounds.[1-3] A particularly well-studied area has been the development of useful synthetic methodologies based upon the reactivity of intermediate metallacyclopentadiene rings formed by intramolecular coupling of two alkyne units at transition-metal centers.[4-6] During our studies of the organometallic

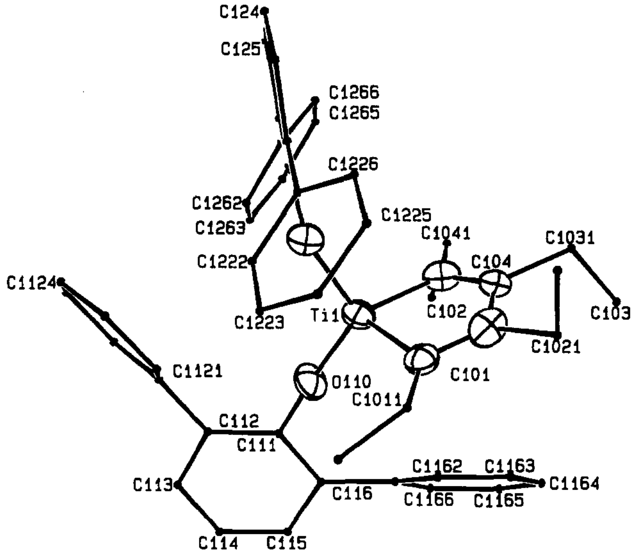

Figure 1. ORTEP view of molecule 1 of $[(Ar''O)_2Ti(C_4Et_4)]$ (1). Selected bond distances (Å) and angles (deg) for molecules 1 and 2: Ti–O(110) = 1.806 (6), 1.788 (6); Ti–O(120) = 1.804 (6), 1.828 (6); Ti–C(101) = 2.016 (9), 1.983 (9); Ti–C(104) = 1.986 (9), 2.02 (1); C(101)–C(102) = 1.35 (1), 1.33 (1); C(102)–C(103) = 1.52 (1), 1.55 (1); C(103)–C(104) = 1.33 (1), 1.34 (1); O(110)–Ti–O(120) = 116.5 (3), 111.1 (3); C(101)–Ti–C(104) = 94.3 (4), 98.5 (4).

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(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; Chapter 9. (b) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, 149. (c) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982. (d) Basset, J. M.; Leconte, M. *CHEMTECH* **1980**, 762.

(2) (a) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342. (b) Wallace, K. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1986**, *5*, 2162. (c) Puddephatt, R. J. *Comments Inorg. Chem.* **1982**, *2*, 69. (d) Schrock, R. R.; McLain, S.; Sancho, J. *Pure Appl. Chem.* **1980**, *52*, 729. (e) Negishi, E.; Takahashi, T. *Synthesis* **1988**, *1*, 1. (f) Yasuda, H.; Tatsumi, K.; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120. (g) Erker, G.; Kruger, C.; Muller, G. *Adv. Organomet. Chem.* **1985**, *18*, 120. (h) Buchwald, S. L.; Wannamaker, M. W.; Watson, B. J. *J. Am. Chem. Soc.* **1989**, *111*, 776. (i) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (j) Lappert, M. F.; Marton, T. R.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 1959. (k) Erker, G.; Dorf, U.; Rheingold, A. L. *Organometallics* **1988**, *7*, 138 and references therein.

(3) (a) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Latesky, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068 and references therein. (b) Curtis, M. D.; Real, J. *J. Am. Chem. Soc.* **1986**, *108*, 4668. (c) Hirpo, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1988**, *110*, 5218. (d) Thorn, D. L.; Hoffman, R. *Nouv. J. Chim.* **1979**, *3*, 39. (e) Upton, T. H.; Rappe, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1982**, *104*, 448. (f) Albers, M. O.; deWaal, P. J. A.; Liles, D. C.; Robinson, D. J.; Singleton, E.; Wiege, M. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1680. (g) Erker, G.; Zwettler, R.; Kruger, C.; Hyla-Kryspin, I.; Gleiter, R. *Organometallics* **1990**, *9*, 524. (h) Hofmann, P.; Frede, M.; Stauffert, P.; Lasser, W.; Thewalt, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *24*, 712. (i) Vaughan, G. A.; Sofield, C. D.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 5491. (j) Petersen, J. L.; Egan, J. W. *Organometallics* **1987**, *6*, 2007.

(4) (a) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1. (b) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (c) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (d) Buchwald, S. L.; Nielson, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870.

0276-7333/90/2309-2211$02.50/0