Materials. Manganese(III) *meso*-tetramesityl chloride[(Mn^{III}(TMP)Cl] was synthesized by literature methods[9] and purified by recrystallization. 4′-(Imidazol-1-yl)acetophenone (NAPI) (Aldrich) was twice recrystallized from methylene chloride/hexane. 4-*tert*-Butylpyridine (4-*t*-BuPy) (Aldrich) and benzyldimethyltetradecylammonium chloride (PTC) (Fluka) were used without further purification. *N*-Phenylimidazole was prepared by literature methods[10] from imidazole and bromobenzene. Saturated hydrocarbons which were used as internal standards were purchased from Aldrich and used without further purification. Olefins (Aldrich) were distilled and passed through neutral alumina columns immediately prior to reaction to remove trace peroxides.

The hypochlorite solution was prepared as follows: 30% LiOCl (3.5 g) purchased from Fluka was dissolved in 50 mL of deionized water. To this solution was added 1.15 g of anhydrous $BaCl_2$ to remove sulfates. The $BaSO_4$ was allowed to settle, and the solution was filtered away from the precipitate. The concentration of LiOCl was ca. 0.3 M, and it was diluted with deionized water to the desired concentration.

Analysis of LiOCl. LiOCl was determined by iodometric titration with standard sodium thiosulfate solution. Dilute LiOCl solutions were determined spectrometrically from the concentration of I_3^- ion (360 nm) formed with sodium iodide.[11]

Analysis of O_2. Mn(TMP)Cl (0.03×10^{-6} mol), PTC (15×10^{-6} mol), and Ph-Im (60×10^{-6} mol) were dissolved with methylene chloride (1.5 mL) in a 4-mL vial sealed by a rubber septum and flushed rigorously with helium. LiOCl (45×10^{-6} mol in 1.5 mL of H_2O) was added, and the mixture was stirred virorously. The reaction was followed by gas chromatographic analysis at room temperature (molecular sieve 5A, activated by baking at 240 °C for 230 h) of the gas layer, and no dioxygen was detected.

Determination of Epoxidation Efficiencies. Typical conditions of epoxidation with a limited amount of lithium hypochlorite were as follows: Mn(TMP)Cl (2.3×10^{-7} mol), PTC (1×10^{-4} mol), N-base (1.1×10^{-4} mol), and olefin ($0.03 \sim 3 \times 10^{-3}$ mol) were dissolved in 10 mL of methylene chloride and stirred vigorously, when lithium hypochlorite aqueous solution (3 mM × 10 mL) was dropped in at room temperature. The complete consumption of hypochlorite required a few minutes to an hour depending upon the olefin and was signalled by a brown-to-green color change of the organic phase. These final solutions have $\lambda_{max} = 478$ nm which indicates the presence of Mn^{III}(TMP)X species.

Stabilities of N-Bases. Stabilities of N-bases were examined in the absence of olefins. Mn(TMP)Cl (5.7×10^{-7} mol), PTC (1×10^{-4} mol), and N-base (1.1×10^{-4} mol) were dissolved in methylene chloride (10 mL). LiOCl solution (20 mL × 0.15 M) was layered on the organic solution, and then the reaction was initiated by vigorous stirring. The reactions were followed by determining the concentration of N-base (gas chromatograph) and the concentration of hypochlorite (iodometric titration). The stabilities of cyclohexanone, cyclohexen-3-ol, cyclohexene epoxide, and 1,2-dihydroxyhexane were examined by the same procedure in the presence of 4-*t*-BuPy.

Stabilities of Catalytic Mixtures: *t*-BuPy. Two solutions each with Mn(TMP)Cl (2.1×10^{-6} mol), PTC (3.8×10^{-4} mol), and *t*-BuPy (4×10^{-4} mol) in 10 mL of CH_2Cl_2 were prepared. Indene (2.1×10^{-3} mol) was added to one, and both solutions were then treated with 36 mL of 0.1 M solution of lithium hypochlorite. The incubation solution was treated with 2.1×10^{-3} mol of indene after 33 min, and the formation of epoxide was followed by GC. The total yield of epoxide was 90 and 91% for the incubated and unincubated cases, respectively.

NAPI. Mn(TMP)Cl (2.3×10^{-7} mol), NAPI (1.1×10^{-4} mol), and PTC (1.1×10^{-4} mol) were dissolved in 10 mL of CH_2Cl_2 and treated with 10 mL of a 3 mM solution of lithium hypochlorite. Iodometry of aliquots taken from the aqueous phase indicated that hypochlorite was consumed within 25 min. Addition of 50 μL of cyclooctene to this mixture led to the formation of *no* epoxide after 80 min. However, when additional lithium hypochlorite (0.1 mL of 0.3 M) was added, cyclooctene oxide was formed, and after 80 min the hypochlorite was again consumed.

Acknowledgment. This work was supported by the National Institutes of Health (5R37-GM18770) and by the National Science Foundation (CHE88-14949).

Unusual Activity and Selectivity in Alkyne Hydrosilylation with an Iridium Catalyst Stabilized by an O-Donor Ligand

Robin S. Tanke* and Robert H. Crabtree

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511.
Received January 29, 1990

Abstract: Catalytic alkyne hydrosilylation has been found for iridium in the O-donor ligand environment of Grim's triso ligand (=tris(diphenyloxophosphoranyl)methanide). The reaction is selective for 1-alkynes and regioselective for β-products and gives the thermodynamically less favored *cis*-vinylsilane products by an unexpected anti addition of Si–H to the triple bond. Mechanistic studies suggest that the alkyne first inserts into the M–Si, not the M–H, bond and that a trans to cis rearrangement occurs via an η^2-vinyl intermediate before reductive elimination. A number of Rh and Ir complexes of the type [(triso)ML_2] are prepared. IR studies on the CO complexes show that the donor power of triso compares with that of other related ligands in an unexpected order: Tp < $P_3O_9^{3-}$ < triso < Cp.

Soft, high-field ligands such as Cp, CO, and PR_3 are used very extensively in homogeneous catalysis and in organometallic chemistry. In contrast, heterogeneous catalysts most commonly employ oxide supports. Yermakov, Schwartz, and others[1] have developed a class of site-isolated oxide-supported catalysts in which a mononuclear organometallic fragment bound to the oxide surface catalyzes various hydrocarbon conversions including alkane functionalization. We have become interested in how the properties of organometallic compounds change on moving to the much less studied O-, N-, and S-donors as supporting ligands, for which very little organometallic chemistry or catalysis is known. We report here some results with an O-donor ligands.

Wolczanski,[2] Chisholm,[3] Klemperer,[4] Finke,[5] Shapley,[6] and others have studied organometallic chemistry in an O-donor ligand environment. These ligands tend to bind most strongly to the oxophilic early and middle transition metals, but complexes of

---

*To whom correspondence should be addressed at the Chemistry Department, Harvard University, Cambridge, MA 02139.

(1) (a) Yermakov, Yu. I.; Kuznetsov, B. N.; Zakharov, V. *Catalysis by Supported Complexes*; Elsevier: Amsterdam, 1981. (b) Ballard, D. G. H. *Adv. Catal.* **1973**, *23*, 263. (c) Schwartz, J. *Acc. Chem. Res.* **1985**, *18*, 302. (d) Gates, B. C.; Lamb, H. H. *J. Mol. Catal.* **1989**, *52*, 1.

(2) LaPointe, R. E.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* **1985**, *4*, 1810.

(3) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. *Chem. Soc. Rev.* **1985**, *14*, 69.

(4) (a) Besecker, C. J.; Klemperer, W. G. *J. Am. Chem. Soc.* **1980**, *102*, 7598. (b) Day, V. W.; Besecker, C. J.; Klemperer, W. G. *Ibid.* **1982**, *104*, 6158. (c) Day, V. W.; Earley, C. W.; Klemperer, W. G.; Maltbie, D. *Ibid.* **1985**, *107*, 8261. (d) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *Ibid.* **1984**, *106*, 4125.

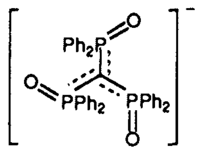
(5) (a) Finke, R. G.; Droege, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7274. (b) Edlund, D. J.; Saxton, R. J.; Lyon, D. K.; Finke, R. G. *Organometallics* **1988**, *7*, 1692.

0002-7863/90/1512-7984$02.50/0

the late transition metals are still relatively rare. Kläui's $[CpCo(R_2PO)_3]^-$,[7] Feher's[8] trisilicate, Klemperer's[9] $P_3O_9^{3-}$, and Grim's[10] triso ligands are good examples of chelating O-donor ligands.

Catalytic chemistry from platinum metal O-donor complexes is known,[11] but in almost all cases the O-ligand is believed either to be ancillary to the P- or C-donor coligand or to dissociate entirely before or during the catalytic reaction. We have now looked at some new iridium complexes of Grim's triso ligand and find that they are highly active hydrosilylation catalysts even at room temperature. The activity and selectivity of these reactions are unusual, some even being of synthetic value.

Finally, we are currently looking for chemically more robust catalyst systems, especially for alkane conversion. A common catalyst deactivation pathway in phosphine complexes involves P–C cleavage.[12] In triso, the P–C bonds are not adjacent to the metal and, therefore, unlikely to be cleaved.



triso$^-$

Preparation and Properties of Ir and Rh Complexes

Few nonlabile O-donor complexes of Rh and Ir are known. Monodentate phosphine oxides[13] do bind but are generally easily displaced even by water or acetone. Kläui[7] has shown that the tridentate O-donor $[CpCo\{(EtO)_2P{=}O\}_3]^-$ (L′) forms isolable coordination and organometallic compounds with a variety of metals, but our attempts to prepare $L'Ir(coe)_2$ from $[Ir(coe)_2Cl]_2$ and $L'Na{\cdot}H_2O$ all failed.[14]

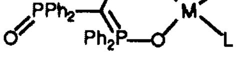
In contrast, we find complexes of the type $(triso)ML_2$ (M = Ir, Rh; L = CO, coe, C_2H_4, $^1/_2$cod; coe = cyclooctene, cod = cyclooctadiene) can be prepared as shown in eqs 1 and 2. First,

$$[ClML_2]_2 + Na[triso] \rightarrow \underset{\textbf{1b–c, 2a}}{(triso)ML_2} \qquad (1)$$

$$\underset{\textbf{2a}}{(triso)Ir(coe)_2} + CO \rightarrow \underset{\textbf{2d}}{(triso)Ir(CO)_2} + coe \qquad (2)$$

$$\underset{\textbf{2a}}{(triso)Ir(coe)_2} + 2C_2H_4 \rightleftarrows \underset{\textbf{2c}}{(triso)Ir(C_2H_4)_2} + 2coe \qquad (3)$$

Na(triso) is generated in situ from NaH and H(triso), subsequent reaction with $[(ol)_2MCl]_2$ in THF at 25 °C generates the alkene complexes **1b–c** and **2a**. Bubbling CO or ethylene through an ether or hexane solution of the bis(cyclooctene) complex **2a** yields the dicarbonyl complex **2d** or the bis(ethylene) complex **2c**. Interestingly, although reaction of **2a** with ethylene proceeds to the right as shown, evaporating the solvent leads to complete reversion to **2a** (eq 3).



1, M = Rh
2, M = Ir
L = coe, **a**; cod, **b**; C_2H_4, **c**; CO, **d**

Table I. ^{31}P NMR Data and P=O Stretching Frequencies

complex	^{31}P NMR (ppm)	ν(P=O), cm^{-1}
H(triso)[10]	24.4 (s)	1183, 1198, 1204
Li(triso)[10]	35.3 (s)	1125, 1136
1b	not obsd	1115, 1159, 1168
2a (C_6D_6)	45.1 (d), 26.0 (t) (J = 21 Hz)	1113, 1151, 1166
2d (C_6D_6)	49.6 (d), 24.2 (t) (J = 23 Hz)	1116, 1169
2c	not obsd	1115, 1161
1c	not obsd	1116, 1156

Table II. Carbonyl Stretching Frequencies

complex	ν(CO), cm^{-1}
$CpIr(CO)_2$[38]	2027, 1987
$TpIr(CO)_2$[39]	2084 (2055), 1999 (1978)
$(triso)Ir(CO)_2$	2070, 1987
$[[(P_3O_9)Ir(CO)_2]^{2-}]$[9c]	2071, 1997

Cyclooctene is much less volatile than ethylene, and so the equilibrium is driven to the left by removal of ethylene in vacuo. Isolation of **2c** was only possible because **2c** is less soluble in hexanes than **2a**. Bubbling ethylene through **2a** suspended in hexanes for 1 h and cooling the mixture at −10 °C under ethylene for several hours gave **2c** as a yellow precipitate.

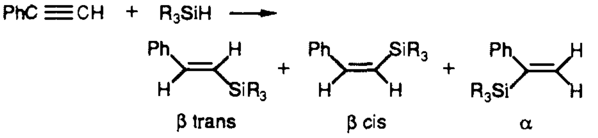
There is often an ambiguity in the hapticity of chelating ligands in Rh(I) and Ir(I) complexes. If triso is η^3, **1** and **2** are 18 electron and trigonal bipyramidal; if η^2, they are 16 electron and square planar. The ^{31}P NMR (Table I) and ^{13}C NMR spectral data for **2a** and **2d** show two distinct types of P atoms and two types of phenyl rings in a 2:1 ratio. This implies that **2a** and **2d** are not fluxional on the NMR time scale and may adopt the square-planar η^2-triso form. **1b,c** and **2d** show only one type of phenyl group by ^{13}C NMR, but the ^{31}P NMR resonances were too broad to be seen at either 298 or 220 K, probably as a result of fluxionality. Grim[15] finds that the η^2-triso form is the most common situation in classical coordination complexes; we therefore propose it for complexes **1** and **2**.

The net electron-donor strength of the series of ligands noted in Table II is in the order Tp < $P_3O_9^{3-}$ < triso < Cp (where Tp is hydrotris(1-pyrazolyl)borate), as judged by the IR ν(CO) data for the iridium dicarbonyl complexes. It is not surprising that the triphosphate with its three negative charges should be more donating than the monoanionic Tp, but it is unexpected that triso, even in the η^2-form, should be more donating than either of these. The IR spectral data (Table I) of complexes **1** and **2** also show bands for the coordinated P=O groups that are shifted little from those of free triso anion.[10,13] A strong IR band at 1113–1116 cm^{-1} is characteristic of all the triso compounds described in this paper.

Catalytic Activity of (Triso)Ir Complexes

Even at ambient temperatures these complexes are efficient catalysts for a variety of reactions such as cyclotrimerization of acetylenes, dehydrogenative silylation of ethylene, and hydrosilylation of terminal acetylenes. In this paper, we describe the alkyne reactions because they go under mild conditions and give an unusual product distribution and because mechanistic studies suggest the intermediacy of an unusual η^2-vinyl intermediate.

Hydrosilylation of Acetylenes. Transition-metal-catalyzed hydrosilylation of 1-alkynes can give a mixture of three products (eq 4). In one, the silicon is bound to the α-carbon of the alkyne.



(4)

---

(6) Zhang, N.; Mann, C. M.; Shapley, P. A. *J. Am. Chem. Soc.* **1988**, *110*, 6591.

(7) Kläui, W.; Müller, A.; Eberspech, W.; Boese, R.; Goldberg, I. *J. Am. Chem. Soc.* **1987**, *109*, 164.

(8) Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 3851.

(9) (a) Besecker, C. J.; Day, V. W.; Klemperer, W. G. *Organometallics* **1985**, *4*, 564. (b) Besecker, C. J.; Klemperer, W. G. *J. Organomet. Chem.* **1981**, *205*, C31. (c) Day, V. W.; Klemperer, W. G.; Lockledge, S. P.; Main, D. J. Personal communication.

(10) Grim, S. O.; Sangokoya, S. A.; Colquhoun, I. J.; McFarlane, W.; Khanna, R. K. *Inorg. Chem.* **1986**, *25*, 2699.

(11) Burk, M. J.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025.

(12) (a) Ortiz, J. V.; Havlas, Z.; Hoffman, R. *Helv. Chim. Acta* **1984**, *67*, 1. (b) Dubois, R. A.; Garrou, P. E.; Lavin, K. D.; Allcock, H. R. *Organometallics* **1984**, *3*, 649. (c) Garrou, P. E. *Chem. Rev.* **1985**, 171.

(13) Goggin, P. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergman Press: New York, 1987; Vol. 2, p 497.

(14) Kläui's ligand (L′) does not form Pt complexes, either; see ref 7.

(15) Grim, S. O. Personal communication, 1990.

Table III. Hydrosilylation with **4**[a]

acetylene	Z:E	yield	turnovers/h
PhCCH	128:1	80‰	68
t-BuCCH	1:2	11%	7.3
$C_5H_{11}CCH$	19:1	39%	34
$HCCCO_2Me$	0:1	trace[b]	

[a] $MeCO_2CCCO_2Me$, PhCCPh, and EtCCEt did not react. [b] 1,2,4-Trimethylbenzene-1,3,5-tricarboxylate is formed.

Table IV. Hydrosilylation with Bis(olefin) Complexes

cat. precursor[a]	Z:E	turnovers/h
(triso)$Ir(C_2H_4)_2$ (**4**)	128:1	68
IndIr(coe)$_2$	52:1	27
$TpIr(C_2H_4)_2$		0
(triso)$Rh(C_2H_4)_2$ (**5**)		0
(Cp-d_5)$Ir(C_2H_4)_2$		0

[a] CH_2Cl_2, 25 °C, PhCCH (1.5 equiv); Et_3SiH (1 equiv); 0.001 mol % catalyst.

In the other two, the Si is attached to the β-carbon, but Si–H addition has taken place in either a syn or an anti manner to give the trans (E) or cis (Z) products, respectively. This lack of selectivity is a drawback in using the reaction for synthetic purposes. We now find that (triso)Ir(coe)$_2$ (**2a**) and (triso)Ir(C_2H_4)$_2$ (**2c**) have several important advantages as catalysts for the hydrosilylation of alkynes. First, they are completely selective for terminal alkynes; internal alkynes such as 3-hexyne, diphenylacetylene, and dimethyl acetylenedicarboxylate do not hydrosilylate. Second, the Si is attached only at the β-C of the alkyne; no detectable α-product is formed. Third, triethylsilane tends to add in the unusual net anti fashion to give the thermodynamically unstable cis compound as the major product, with a Z:E ratio that can be as high as 190:1. In contrast, triphenylsilane gives a product mixture[16] that favors the trans (E) isomer, and from which the E isomer can be obtained pure. The homogeneity of the catalyst was confirmed by the mercury test.[17] There is no evidence for an induction period, and the catalyst is stable for at least 20 h in CD_2Cl_2.

Table III reports the results of the catalytic studies and shows that Z:E ratios and turnover rate depend on the substrate used. If the acetylene binds too strongly to the catalyst, no hydrosilylation is observed, as is found for dimethyl acetylenedicarboxylate. Methyl propiolate undergoes cyclotrimerization[18] instead of hydrosilylation. 3-Hexyne fails to undergo hydrosilylation because it fails to interact with the catalyst. For phenylacetylene, 3,3-dimethyl-1-butyne, and 1-heptyne, the variation in the the Z:E ratio is likely due to the fact that **2c** in the presence of silane is an olefin isomerization catalyst. β-(Triethylsilyl)styrene (100 equiv, Z:E = 190:1) in contact with **2c** (1 equiv) and triethylsilane (5 equiv) converts to β-(triethylsilyl)styrene having a Z:E ratio of 11:1 in only 5 min at 25 °C, much faster than isomerization occurs in catalytic alkyne hydrosilylation. The presence of acetylene therefore diminishes the rate of olefin isomerization, and hydrosilylation is favored over the competitive isomerization pathway, so the observed Z:E ratio is high. It is not surprising that phenylacetylene has a higher Z:E ratio and turnover rate than 1-heptyne and 3,3-dimethyl-1-butyne. Phenylacetylene is a better ligand on both steric and electronic grounds and so inhibits isomerization. In addition, the formation of cis (Z) isomers of *tert*-butylolefins is extremely rare, even in free-radical-catalyzed hydrosilylation of alkynes where cis isomers often dominate, no (Z)-3,3-dimethyl-1-(triethylsilyl)butene is observed from 3,3-dimethyl-1-butyne.[19]

The role of triso in promoting the catalytic activity of the metal is illustrated in Table IV, which shows that Ir complexes containing related C- and N-donor ligands such as Cp and Tp[20] fail to catalyze the reaction of triethylsilane with phenylacetylene. We find one exception, IndIr(coe)$_2$,[21] which does act as a catalyst, although the rate and selectivity observed are not as good as for the triso complex. This makes us suspect that there may be a mechanistic analogy between the two systems. One of the key features of indenyl chemistry is its ability to slip from the η^5 to the η^3 form, something both we[22] and others[21] have noted. In our study of (triso)Ir chemistry, both η^3 and η^2 forms seem possible.[23] The point in common between the indenyl ligand and triso is the ability to rearrange in such a way as to create a 2-electron hole in the metal valence shell or accommodate the arrival of a 2-electron ligand. This flexibility may therefore be important in the catalytic activity of the system.

Base-catalyzed and free-radical-initiated hydrosilylations often give cis products, but rarely with selectivities greater than 2:1 (Z:E).[20] Z:E selectivities as high as 5:1 have been observed in the hydrosilylation of alkynes with Wilkinson's catalyst[24] and with other Rh(I) and Ir(I) complexes.[25] Ojima[26] has found Rh catalysts with high Z:E ratios in work done at the same time as ours.

Mechanistic Studies

We have considered six mechanisms (Scheme I) that seem to have the best chance of producing high Z:E ratios, many of which have previously been considered in other hydrosilylation reactions. Others can be envisaged,[27] but none of these seem plausible. For example, electron transfer from the metal to the alkyne is unlikely because electrochemical studies show that the (triso)Ir(I) complex **2a**, alone or in the presence of triethylsilane and phenylacetylene, has only an irreversible reduction at −1.4 V in CH_2Cl_2 in the range between +2 and −2 V versus AgCl on a glassy carbon electrode.

Of the six most reasonable mechanisms A–F, we have been able to exclude all but mechanism E, which we therefore propose. Ojima[26] has independently come to an essentially similar conclusion for his case. Mechanism A is said to account for the formation of cis products with Wilkinson's catalyst.[24a,b] It involves initial formation of the expected product of syn addition, the *trans*-vinylsilane, followed by trans to cis isomerization. While this is adequate to explain the formation of small amounts of cis product, it cannot be invoked in our case because the thermodynamic equilibrium must favor the less hindered trans compound.

---

(16) Crude ^1H NMR indicated ca. 1:1 mixture of E and Z isomers, but distillation at 200 °C (ca. 0.1 Torr) gave only the E isomer.

(17) (a) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855. (b) Whitesides, G. M.; Hackett, M.; Brainard, R. L.; Lavalleye, J.-P. P. M.; Souinski, A. F.; Izumi, A. N.; Moore, S. S.; Brown, D. W.; Staudt, E. M. *Organometallics* **1985**, *4*, 1819.

(18) Complexes **2a** and **2c** are catalysts for acetylene cyclotrimerization. Tanke, R. S.; Crabtree, R. H. Unpublished results.

(19) Benkeser, R. A.; Ehler, D. F. *J. Organomet. Chem.* **1974**, *69*, 193.

(20) Tanke, R. S.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3444.

(21) Merola, J. S.; Kacmarcik, R. T.; Engen, D. V. *J. Am. Chem. Soc.* **1986**, *108*, 2460.

(22) Habib, A.; Tanke, R. S.; Holt, E. M.; Crabtree, R. H. *Organometallics* **1989**, *8*, 1225.

(23) (a) Ir(III) and Ir(V) complexes with an η^3-triso ligand have been prepared. Tanke, R. S.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1056. (b) η^3–η^2 triphos (=$MeC(CH_2PPh_2)_3$) conversion has been shown in hydroformylation reactions: Thaler, E. G.; Folting, K.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 2664.

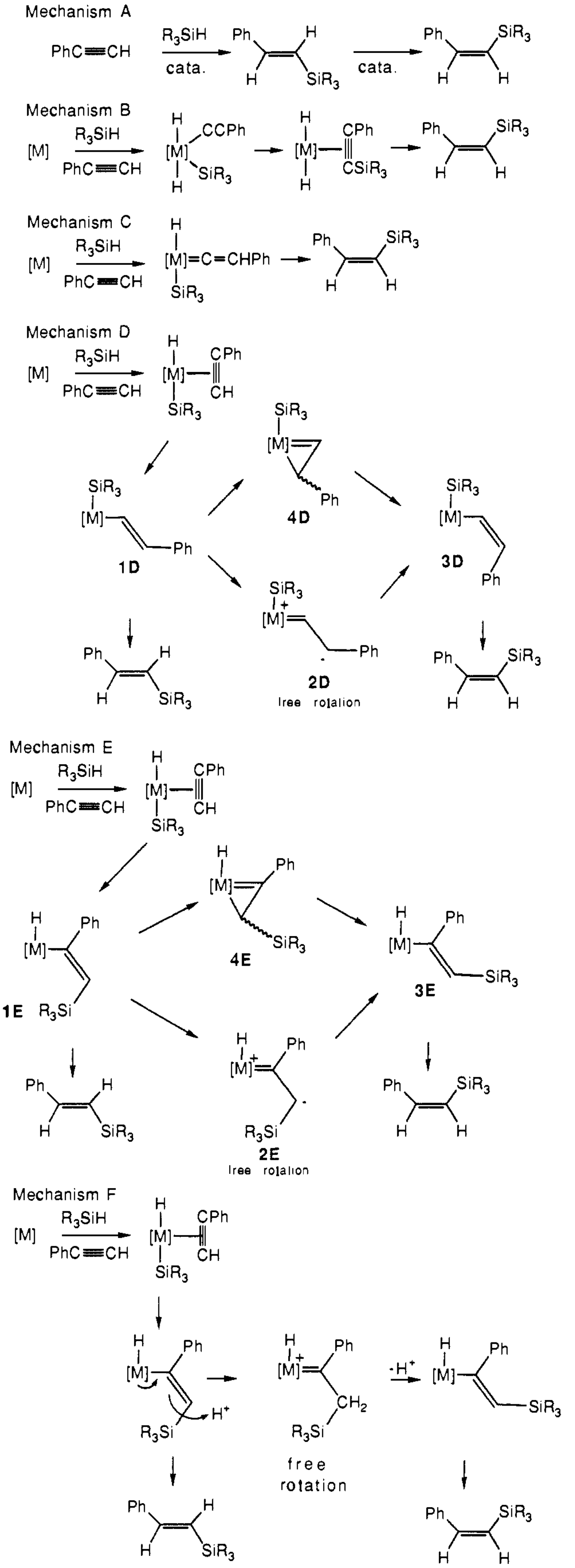
(24) (a) Brady, K. A.; Nile, T. A. *J. Organomet. Chem.* **1981**, *206*, 299. (b) Dickers, H. M.; Haszeldine, R. N.; Mather, A. P.; Parish, R. V. *J. Organomet. Chem.* **1978**, *161*, 91. (c) Ojima, I.; Kumagai, M.; Nagai, Y. *J. Organomet. Chem.* **1974**, *66*, C14.

(25) (a) Brockmann, M.; tom Dieck, H.; Klaus, J. *J. Organomet. Chem.* **1986**, *301*, 209. (b) Lappert, M. F.; Maskell, R. K. *Ibid.* **1984**, *264*, 217. (c) Apple, D. C.; Brady, K. A.; Chance, J. M.; Heard, N. E.; Nile, T. A. *J. Mol. Catal.* **1987**, *42*, 195.

(26) For a recent review of hydrosilylation see: (a) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 1479. (b) Ojima, I. Personal communication, 1990. (c) Ojima, I.; Ingallina, P.; Clos, N. 199th National Meeting of the American Chemical Society, Boston MA, Spring 1990; American Chemical Society: Washington, DC, 1990; INORG 197, 205, 206; XII Organosilicon Symposium, Philadelphia, PA, Apr 7,8 1989; *Organometallics*, submitted for publication.

(27) (a) A reviewer has suggested that the real catalyst is a dihydride formed by hydrolysis or disproportionation of the silyl hydride. The acetylene is hydrogenated to give a bound alkene that undergoes dehydrogenative silylation. We can eliminate this possibility because we find the appropriate alkenes do interact with the catalyst but only to give isomerization and not dehydrogenative silylation. A full account of this work has been submitted.[27b] (b) Tanke, R. S.; Crabtree, R. H. *Organometallics*, in press.

Scheme I. Proposed Mechanisms for Cis Hydrosilylation



We have examined the isomerization experimentally by contacting *cis*-PhCD=CD(SiEt$_3$) with **2c** and Et$_3$SiH. The cis to trans isomerization does indeed occur because protio-labeled trans product appears. The back-reaction is *not* observed: the cis compound does not incorporate protio label, which would happen if the protio-labeled trans product isomerized back to the cis form.

Any isomerization in A therefore acts to lower the *Z*:*E* ratio, not increase it. We find that the highest *Z*:*E* ratios are observed at high alkyne concentrations. This suggests that the presence of alkyne inhibits the isomerization, which is in full accord with the results discussed previously.

Mechanisms B and C were ruled out by deuterium-labeling studies. In B, a silylalkyne is formed and hydrogenated, and in C, a metalacumulene is invoked. Reaction of PhC≡CD and Et$_3$SiH in the presence of **2c** yielded only the d_1-cis product with the deuterium at the same β position as in the starting PhC≡CD. (The assignment of protons was confirmed by NOE.) Hence, there is no C–D bond cleavage. Mechanism B, which should scramble the D label, and C, which should cause it to shift to the α position both involve C–D bond cleavage and can be ruled out.

Mechanisms D and E are related, and both involve alkyne insertion. In D, the alkyne initially inserts into the M–H bond, and in E it inserts into the M–Si bond. The initial *cis*-vinyl insertion product isomerizes *on the metal*, so the thermodynamics of the free *Z* and *E* isomers are irrelevant to the position of equilibrium for the bound vinyl species. Only in mechanism E can we understand how the cis product can be favored to the extent observed in our studies. The position of equilibrium between **1E** and **3E** (in Scheme I, mechanism E) must favor **3E**, because this is the isomer that goes on to give the observed cis product. The thermodynamics of **1E** and **3E** determines the equilibrium constant, and the only substantial differences between the two isomers are steric. Steric effects clearly favor **3E** if the metal and other ligands, represented as [M] in the scheme, are more bulky than the SiR$_3$ group, as is reasonable. On the other hand, in mechanism D the equilibrium between **1D** and **3D** should favor **1D**, which would go on to give the unobserved trans vinylsilane. D is therefore ruled out.

This means that the initial alkyne insertion must take place into the M–Si bond (mechanism E) to the almost complete exclusion of insertion into the M–H bond (D). In hydrosilylation, there has long been discussion about whether the first insertion takes place into the M–H or the M–Si bond. Here we have a situation where a real distinction can be made. Although insertion of an unsaturated group into an M–Si bond has been shown previously,[28] ours seems to be the first case in which this pathway is found to dominate over insertion into M–H.

Mechanism D has been proposed before,[25c] but the isomerization step has been considered to involve the formation of a dipolar intermediate (e.g., **2D** and **2E**),[29] which allows rotation about what was the vinyl C=C bond. We are not convinced that **2E** is likely. No persuasive evidence for the existence of such an unusual intermediate has ever been gathered. An alternative structure (e.g., **4E**) seems to us to be far more likely. Green et al.[30] have shown that when an η^1-vinyl is formed in a coordinatively unsaturated environment, it can rearrange to the η^2-form. This form (**4D** and **4E**) can open to give either the cis or the trans η^1-form. The R group is never scrambled between the 1- and 2-positions of the vinyl by this process. This provides a mechanism for the cis/trans interconversion based on a known intermediate. The initially formed η^1-vinyl must be in a coordinatively unsaturated environment because the electron count of the system falls by 2 on undergoing the insertion, and conversion to the η^2-form allows the metal to regain the 18-electron configuration.

Reductive elimination to give product cannot take place directly from **4E**, however, because there would then be no reason for the high cis to trans ratio observed; if anything, trans should be favored. This requires that **4E** is only an intermediate serving to equilibrate **1E** and **3E** and that this equilibration is fast relative to reductive elimination. Less likely, reductive elimination in **3E** might be much faster than in **1E**. Except for proposing the η^2-vinyl intermediate, Ojima[26] has come to very similar conclusions.

---

[28] Randolph, C. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3366.

[29] Hart, P. W.; Schwartz, J. *J. Organomet. Chem.* **1975**, *87*, C11.

[30] Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1985**, 435.

We considered a possible alternative version of mechanism E that avoids the carbanion (mechanism F), in which trace acid causes isomerization by protonating the vinyl, but we find that the reaction is unaffected by the presence of a trace of triethylamine in benzene. We can therefore rule out mechanism F.

Conclusion

We have studied the influence of an O-donor ligand on organometallic chemistry and catalysis with iridium. We have demonstrated the first example of hydrosilylation with an O-donor ligand, where homogeneity of the catalyst has been verified. Unusual selectivity patterns are observed; most notably, the hydrosilylation of terminal acetylenes gives high selectivities for the unexpected cis isomer. The results are interpreted in terms of initial alkyne insertion into M–Si, rather than M–H bonds.

Experimental Section

General Procedures. All manipulations were carried out in an argon atmosphere with standard Schlenk techniques. NMR spectra were recorded on a Bruker WM-250 or a Bruker WM-500 spectrometer at ambient temperature unless otherwise indicated. $^{31}P\{^1H\}$ NMR were recorded with 85% H_3PO_4 as the reference. IR spectra were recorded on a Nicolet S-SX FT spectrometer. Combustion analyses were performed by Galbraith Laboratories or Desert Analytics.

Tetrahydrofuran (THF), ether, toluene, and hexanes were distilled from sodium benzophenone ketyl and dichloromethane from calcium hydride. Tris(diphenylphosphinyl)methane was prepared according to Grim et al.[10] $[(coe)_2IrCl]_2$ was prepared[31] from ammonium hexachloroiridate. Phenylacetylene was purchased from Aldrich and distilled before use. All other reagents were used as received. Phenylacetylene (92% d_1) was prepared by deprotonation of the d_0 isotopomer with *n*-BuLi and quenching with D_2O. Triethylsilane-d_1 (Si–D) was prepared by refluxing the corresponding chlorosilane with lithium aluminum deuteride in ether for 8 h.

[Tris(diphenyloxophosphoranyl)methanido](η^4-cyclooctadiene)rhodium(I) (1b). Sodium hydride (8 mg, 0.18 mmol, 60% oil dispersion) was washed with hexanes (3×) and suspended in THF (10 mL). H(triso) (100 mg, 0.16 mmol) was added and gas evolution observed. $[(cod)RhCl]_2$[32] (40 mg, 0.08 mmol) was then added, and the mixture was stirred at 25 °C for 4 h and then filtered over Celite. The volume was reduced to ca. 4 mL, and hexanes were added to afford a white precipitate. Recrystallization from CH_2Cl_2/hexanes yielded **1b** (85 mg, 63% yield). ^1H NMR (CD_2Cl_2, 250 MHz): δ 7.85–7.75 (m, 12 H, Ph), 7.4–7.2 (m, 18 H, Ph), 3.9 (b, 4 H, cod vinyl), 2.5 (b, 4 H, cod allyl), 1.8 (b, 4 H, cod allyl). ^{13}C NMR (CD_2Cl_2, 62.98 MHz): δ 136.8 (q, J_{P-C} = 112 Hz, C_{Ph}–P), 132.7 (d, J_{P-C} = 9 Hz, Ph), 130.4 (*p*-Ph), 127.6 (d, J_{P-C} = 12 Hz, Ph), 76.1 (d, J_{Rh-C} = 15 Hz, cod vinyl), 31.02 (cod allyl). ^{31}P NMR: not observable at 298 or 220 K. IR (Nujol): 1168, 1159, 1115 (s) cm^{-1} (ν(P=O)). Anal. Calcd for $C_{45}H_{42}P_3O_3Rh\cdot1.4CH_2Cl_2$: C, 58.93; H, 4.78. Found: C, 58.77; H, 5.00.

[Tris(diphenyloxophosphoranyl)methanido]bis(ethylene)rhodium(I) (1c). To Na(triso) (prepared from sodium hydride (24 mg, 0.09 mmol, 60% oil dispersion) and H(triso) (50 mg, 0.08 mmol) in THF (10 mL)) was added $[(C_2H_4)_2RhCl]_2$[33] (29 mg, 0.04 mmol). The mixture was stirred for 2.5 h at 25 °C, solvent was removed in vacuo, and the residue was dissolved in ether (30 mL) and filtered over Celite. The yellow ether solution was reduced to ca. 5 mL, and hexanes were added to afford a precipitate, which was filtered and recrystallized from CH_2Cl_2/hexanes to yield **5** (20 mg, 32% yield). ^1H NMR (C_6D_6, 250 MHz): δ 8.0 (m, 12 H, Ph), 7.0 (m, 18 H, Ph), 2.0 (m, 8 H, ethylene). ^{13}C NMR (C_6D_6, 62.98 MHz): δ 137.1 (d, J_{P-C} = 114 Hz, C–P), 132.9 (d, J_{P-C} = 10 Hz, Ph), 130.1 (Ph), 127.4 (Ph), 58.6 (d, J_{Rh-C} = 15 Hz, ethylene). ^{31}P NMR: not observable at 298 K. IR (C_6D_6): 1156, 1116 (ν(P=O)) cm^{-1}. Anal. Calcd for $C_{41}H_{38}O_3P_3Rh$: C, 63.57; H, 4.95; P, 12.00. Found: C, 63.21; H, 4.97; P, 12.09.

[Tris(diphenyloxophosphoranyl)methanido]bis(η^2-cyclooctene)iridium(I) (2a). Na(triso) was prepared as above from sodium hydride (28 mg, 0.49 mmol, 60% oil dispersion) and H(triso) (300 mg, 0.49 mmol) in THF (30 mL). $[(coe)_2IrCl]_2$ (218 mg, 0.234 mmol) was added, and the orange solution was stirred at 25 °C for 4 h. CH_2Cl_2 was removed in vacuo, ether (50 mL) was added, and the mixture was filtered over Celite to remove salts. The ether was removed in vacuo and the resultant yellow powder recrystallized from CH_2Cl_2/hexanes. Filtration and drying in vacuo yielded **2a** (380 mg, 76% yield). ^1H NMR ($CDCl_3$, 250 MHz): δ 7.9–7.7 (m, 8 H, Ph), 7.4–7.0 (m, 22 H, Ph), 1.2–2.0 (m, 28 H, coe). ^{13}C NMR ($CDCl_3$, 62.98 MHz): δ 138.8 (d, J_{P-C} = 110 Hz, C_{Ph}–P), 134.8 (d, J_{P-C} = 113 Hz, C_{Ph}–P), 132.7 (d, J_{P-C} = 11 Hz, Ph), 132.1 (d, J_{P-C} = 10 Hz, Ph), 130.4 (*p*-Ph), 129.4 (p-Ph), 127.2 (d, J_{P-C} = 13 Hz, Ph), 127.1 (d, J_{P-C} = 13 Hz, Ph), 61.8 (vinyl coe), 56.4 (coe vinyl), 29.4, 28.0, 26.8, 26.7, 26.5, 26.3 (coe). ^{31}P NMR (C_6D_6, 202.45 MHz): δ 45.05 (d, 2 P, J_{P-P} = 21 Hz), 26.0 (t, 1 P). IR (Nujol): 1166, 1151, 1113 (s) cm^{-1} (ν(P=O)). Anal. Calcd for $C_{53}H_{59}P_3O_3Ir\cdot0.33CH_2Cl_2$: C, 60.57; H, 5.68. Found: C, 60.57; H, 5.57.

[Tris(diphenyloxophosphoranyl)methanido]bis(ethylene)iridium(I) (2c). Ethylene (20 mL/min) was bubbled through a hexane solution (30 mL) of **2** (prepared as above from H(triso) (400 mg, 0.65 mmol), $[(coe)_2IrCl]_2$ (291 mg, 0.33 mmol), and NaH (32 mg, 0.68 mmol)) for 1 h. The solution was held at −10 °C for 3 h, yielding a yellow precipitate that was filtered and dried in vacuo. Recrystallization from CH_2Cl_2/hexanes yielded **2c** (366 mg, 65% yield). ^1H NMR (CD_2Cl_2, 250 MHz, 200 K): δ 7.75–7.55 (m, 8 H, Ph), 7.4–7.0 (m, 22 H, Ph), 3.02 (m, 4 H, ethylene), 1.89 (m, 4 H, ethylene). ^1H NMR ($CDCl_3$, 250 MHz, 327 K): δ 7.75–7.55 (m, 8 H, Ph), 7.4–7.0 (m, 22 H, Ph), 2.5 (s, 8 H, ethylene). ^{13}C NMR ($CDCl_3$, 62.98 MHz): δ 134.9 (d, J_{P-C} = 110 Hz, C–P), 132.2 (d, J_{P-C} = 11 Hz, Ph), 130.2 (*p*-Ph), 127.3 (d, J_{P-C} = 13 Hz, Ph), 38.5 (ethylene). ^{31}P NMR: not observable at 298 or 220 K. IR (Nujol): 1161, 1115 cm^{-1} (ν(P=O)). Anal. Calcd for $C_{41}H_{39}O_3P_3Ir\cdot0.25CH_2Cl_2$: C, 55.99; H, 4.39. Found: C, 56.01; H, 4.56.

[Tris(diphenyloxophosphoranyl)methanido]dicarbonyliridium(I) (2d). CO (20 mL/min) was bubbled through an ether solution (20 mL) of **2a** (0.097 mmol, 100 mg) for 20 min until the solution became colorless. The volume of solvent was reduced to ca. 4 mL, and hexanes were added to afford a white precipitate. Recrystallization from benzene/hexanes gave **2d** (77 mg, 88% yield). ^1H NMR ($CDCl_3$, 250 MHz): δ 7.6–7.7 (m, 8 H, Ph), 7.4–7.3 (m, 10 H, Ph), 7.2–7.1 (m, 10 H, Ph), 7.0 (dt, 2 H, Ph). ^{13}C NMR ($CDCl_3$, 62.98 MHz): δ 166.6 (2 C, CO), 136.6 (d, J_{P-C} = 110 Hz, C_{Ph}–P), 132.6 (d, J_{P-C} = 113 Hz, *C*–P), 132.5 (d, J_{P-C} = 11 Hz, Ph), 131.8 (d, J_{P-C} = 10 Hz, Ph), 129.7 (*p*-Ph), 127.6 (*p*-Ph), 127.5 (d, J_{P-C} = 16 Hz, Ph), 127.4 (d, J_{P-C} = 12 Hz, Ph). ^{31}P NMR (C_6D_6, 202.45 MHz): δ 49.6 (d, 2 P, J_{P-P} = 23 Hz), 24.2 (t, 1 P). IR (Nujol): 2070, 1987 (C=O), 1169, 1116 cm^{-1} (P=O). Anal. Calcd for $C_{39}H_{30}O_5P_3Ir$: C, 54.22; H, 3.50. Found: C, 54.04; H, 3.50.

Hydrosilylation Reactions with 2c. β-(Triethylsilyl)styrene.[24a] A dry Schlenk tube was charged with **2c** (10 mg, 0.012 mmol), triethylsilane (1.9 mL, 11.6 mmol), phenylacetylene (1.9 mL, 17.4 mmol), and CH_2Cl_2 (5 mL). The mixture was stirred at 25 °C for 12.5 h. Volatiles were removed in vacuo. The mixture was transferred to a round-bottom flask and the product distilled (80 °C (ca. 0.1 Torr)) to yield β-(triethylsilyl)styrene (*Z*:*E* = 128:1, 2 g, 80% yield, 829 turnovers, 62 turnovers/h). The ^1H NMR assignment was confirmed by NOE. ^{13}C NMR ($CDCl_3$, 62.98 MHz): δ 147.8 (d), 140.5 (s), 129.3 (d), 127.8, 127.7, 127.3, 7.5 (q), 4.8 (t). This reaction is unaffected by addition of mercury (400 mg, 2 mmol) but is inhibited by dimethyl acetylenedicarboxylate or pyridine (10 equiv/1 equiv of **2b**). Complex **2a** is also a catalyst for this reaction. The reactions proceed with similar selectivity and rate in benzene (10 mL) or in benzene containing triethylamine (10 mL, 0.1% v/v).

3,3-Dimethyl-1-(triethylsilyl)-1-butene.[34] A dry Schlenk tube was charged with **2c** (9 mg, 0.01 mmol), triethylsilane (0.6 mL, 3.7 mmol), 3,3-dimethyl-1-butyne (0.5 mL, 4.0 mmol), and CH_2Cl_2 (5 mL). The mixture was stirred at 25 °C for 5.2 h. Volatiles were removed in vacuo. The mixture was transferred to a round-bottom flask and the product distilled (40 °C (ca. 0.1 Torr)) to yield 3,3-dimethyl-1-(triethylsilyl)-1-butene (*Z*:*E* = 1:2, 80 mg, 11% yield, 38.7 turnovers, 7.5 turnovers/h).

1-(Triethylsilyl)-1-heptene.[35] A dry Schlenk tube was charged with **2c** (20 mg, 0.023 mmol), triethylsilane (3.7 mL, 23 mmol), 1-heptyne (6 mL, 46 mmol), and CH_2Cl_2 (5 mL). The mixture was stirred at 25 °C for 11 h. Volatiles were removed in vacuo. The mixture was transferred to a round-bottom flask and the product distilled (68 °C (ca. 0.1 Torr)) to yield 1-(triethylsilyl)-1-heptene (*Z*:*E* = 19:1, 1.9 g, 39% yield, 388 turnovers, 33.8 turnovers/h). ^{13}C NMR (62.98 MHz, $CDCl_3$): δ 150.33, 125.02, 34.1, 31.7, 29.7, 22.7, 13.9, 7.42, 4.9.

Attempted Preparation of Methyl 2-(Triethylsilyl)acrylate.[24a] A dry Schlenk tube was charged with **2c** (5 mg, 0.006 mmol), triethylsilane (0.93 mL, 5.76 mmol), methyl propiolate (0.77 mL, 8.7 mmol), and CH_2Cl_2 (5 mL). The mixture was stirred at 25 °C for 8.5 h. Volatiles were removed in vacuo, and ^1H NMR data showed peaks identical with 1,3,5- (and 1,2,4-) trimethylbenzenetricarboxylate (the alkyne cyclotrimerization product) and a trace amount of (*E*)-methyl-2-(triethylsilyl)acrylate.

---

(31) Onderdelinden, A. L. *Inorg. Synth.* **1974**, *15*, 18.
(32) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.
(33) Cramer, R. *Inorg. Synth.* **1974**, *15*, 14.
(34) Voronkov, M. G.; Ushakova, N. I.; Tsykhanskaya, I. I.; Pukhnarevich, V. B. *J. Organomet. Chem.* **1984**, *264*, 39.
(35) Tsipis, C. A. *J. Organomet. Chem.* **1980**, *187*, 427; *188*, 53.

β-(Triphenylsilyl)styrene.[36] A dry Schlenk tube was charged with **2c** (17 mg, 0.012 mmol), triphenylsilane (3.9 g, 15 mmol), phenylacetylene (2.2 mL, 19.7 mmol), and CH_2Cl_2 (5 mL). The mixture was stirred at 25 °C for 11 h. The ^1H NMR of the crude material showed evidence of *Z* product (approximately 1:1 mixture); however, the mixture was distilled (200 °C (ca. 0.1 Torr)) to yield only (*E*)-β-(triphenylsilyl)-styrene (1.6 g, 25% yield).

Reactions with Other Bis(olefin) Complexes. Complexes **1c**, $TpIr(C_2H_4)_2$, and $(Cp\text{-}d_5)Ir(C_2H_4)_2$[37] were not catalyst precursors for the hydrosilylation of phenylacetylene with triethylsilane at 25 °C in CH_2Cl_2. Both **1c** and $TpIr(C_2H_4)_2$ undergo reaction with the silane/alkyne mixture but do not catalyze the hydrosilylation. $(Cp\text{-}d_5)Ir(C_2H_4)_2$ remains unchanged under the reaction conditions. $IndIr(coe)_2$ is a catalyst for the reaction, but it proceeds more slowly than reactions catalyzed by **2a**.

Catalysis with $IndIr(coe)_2$. A dry Schlenk tube was charged with $IndIr(coe)_2$ (13 mg, 0.023 mmol), triethylsilane (3.7 mL, 23.2 mmol), phenylacetylene (3.7 mL, 33.7 mmol), and CH_2Cl_2 (5 mL). The mixture was stirred at 25 °C for 7.5 h. The mixture was transferred to a round-bottom flask and the product distilled (80 °C (ca. 0.1 Torr)) to yield β-(triethylsilyl)acetylene (*Z*:*E* = 52:1, 1.02 g, 20% yield, 203 turnovers, 27 turnovers/h).

Deuterium Labeling Studies. β-Deuterio-β-(triethylsilyl)styrene (92% *d*). A dry Schlenk tube was charged with **2c** (10 mg, 0.012 mmol), triethylsilane (0.67 mL, 4.1 mmol), phenylacetylene (92% PhC≡CD, 0.6 mL, 2.2 mmol), and CH_2Cl_2 (5 mL). The mixture was stirred at 25 °C for 4.5 h. Volatiles were removed in vacuo. The mixture was transferred to a round-bottom flask and the product distilled (80 °C (ca. 1 Torr)) to yield β-deuterio-β-(triethylsilyl)styrene (92% d_2). ^2H NMR ($CHCl_3$, 76.77 Hz): δ 5.83 (d, J_{H-D} = 1.8 Hz). ^1H NMR shows about 8% β-(triethylsilyl)styrene by integration.

A dry Schlenk tube was charged with **2c** (11 mg, 0.013 mmol), triethylsilane (>99% R_3SiD, 0.67 mL, 4.1 mmol), phenylacetylene (92% PhC≡CD, 0.58 mL, 2.1 mmol), and CH_2Cl_2 (5 mL). The mixture was stirred at 25 °C for 4.5 h. Volatiles were removed in vacuo. The mixture was transferred to a round-bottom flask and the product distilled (80 °C (ca. 1 Torr)) to yield α,β-dideuterio-β-(triethylsilyl)styrene (92% d_2). ^2H NMR ($CHCl_3$, 76.77 Hz): δ 7.49 (s), 5.83 (s). ^1H NMR shows about 8% α,β-dideuterio-β-(triethylsilyl)styrene by integration.

Acknowledgment. We thank the NSF for funding. NMR spectra were obtained at the Northeast Regional NSF/NMR Facility at Yale University. We gratefully acknowledge Dr. P. Demou for NMR assistance, Dr. M. Zimmer for electrochemical studies, Prof. S. O. Grim for useful discussions, and Prof. I. Ojima for sharing his results with us.

---

[36] Brook, A. G.; Duff, J. M.; Renyolds, W. F. *J. Organomet. Chem.* **1976**, *121*, 293.

[37] We thank Neil Payne for a gift of $(Cp\text{-}d_5)Ir(C_2H_4)_2$.

[38] Fisher, E. O. et al. *Z. Naturfosch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1962**, *17*, 77.

[39] Hoyano, J. K.; Graham, W. A. G. 195th National Meeting of the American Chemical Society, Toronto, Canada, American Chemical Society: Washington, DC, 1988, INORG 216.

Ladder Structure of $[(^tBuCH_2)_2TaN]_5{\cdot}NH_3{\cdot}2C_7H_8$ and Its Relationship to Cubic TaN

Mark M. Banaszak Holl,[†] **Peter T. Wolczanski,***[‡] **and Gregory D. Van Duyne**

Contribution from the Cornell University, Department of Chemistry, Baker Laboratory, Ithaca, New York 14853. *Received December 18, 1989*

Abstract: Ammonolysis of $(^tBuCH_2)_3Ta{=}CH^tBu$ (**1**) at 20 °C produced an intermediate pentamer, $[(^tBuCH_2)_2TaN]_5$ (**2**, ~40%); further reaction generated an orange precipitate. Thermolysis of the latter at 400 °C and then 820 °C produced cubic TaN (*Fm3m*, a = 4.300 (2) Å) at temperatures and pressures substantially below those of conventional nitriding procedures. Ammonolysis of $(^tBuCH_2)_2Ta(NMe_2)_3$ (**3**) provided an alternative (19%), route to **2**. ^1H, ^{13}C, and ^{15}N NMR spectra of **2** indicated C_{2v} symmetry, and X-ray crystallographic characterization of $[(^tBuCH_2)_2TaN]_5{\cdot}NH_3{\cdot}2C_7H_8$ ($\mathbf{2}{\cdot}NH_3{\cdot}2C_7H_8$) revealed a roughly planar ladder structure of alternating $(^tBuCH_2)_2TaN$ units. The interior nitrogens adopt a T-shaped coordination geometry and an NH_3 is weakly bound to an exterior Ta atom. Crystal data ($\mathbf{2}{\cdot}NH_3{\cdot}2C_7H_8$): triclinic $P\bar{1}$, λ(Mo Kα), μ = 7.068 mm^{-1}, a = 11.616 (2) Å, b = 15.407 (3) Å, c = 23.172 (6) Å, α = 106.120 (17)°, β = 99.060 (18)°, γ = 100.170 (16)°, T = -20 °C, Z = 2, V = 3829.6 (12) Å^3, R = 0.083, R_w = 0.098, 7346 (72.8%) reflections where $|F_o| \geq 3\sigma(F_o)$. The conformation of $\mathbf{2}{\cdot}NH_3{\cdot}2C_7H_8$ reflects the motif of cubic TaN, rather than the thermodynamically expected hexagonal form, hence the framework of this ceramic may be dictated by the geometry of the molecular precursor.

Introduction

Organotransition-metal complexes are promising as precursors in the formation of solid-state materials.[1] Solution methods leading to aggregates, solids,[2-4] and polymeric materials[5-7] are inherently advantageous because the conditions employed are mild relative to conventional solid-state syntheses. Potential advances include low-temperature routes to known compounds in addition to the rational design of new, kinetically stable materials.

Recently, thermolysis of "$TaN_xH_{(3x-5)}$", a precipitate derived from ammonolysis of $(^tBuCH_2)_3Ta{=}CH^tBu$ (**1**),[8] was shown to yield cubic tantalum nitride (*Fm3m*, a = 4.300 (2) Å) via the sequence in eqs 1 and 2.[9] According to the Ta/N phase diagram,[10] hexagonal tantalum nitride (*P6/mmm*)[11] is the expected thermodynamic product under the conditions employed. The

$$\underset{\mathbf{1}}{(^tBuCH_2)_3Ta{=}CH^tBu} + xNH_3 \xrightarrow[(2)\ C_6D_6,\ 100\ °C,\ 2\ days]{(1) C_6H_6,\ 20\ °C,\ 2\ days} TaN_xH_{(3x-5)} + {\sim}4CMe_4 \quad (1)$$

$$TaN_xH_{(3x-5)} \xrightarrow[24\ h]{400\ °C} \underset{(amorphous)}{TaN} \xrightarrow[3\ days]{820\ °C} \underset{(Fm3m)}{\delta\text{-}TaN} \quad (2)$$

[†] IBM Graduate Research Fellow 1990-1991.

[‡] Alfred P. Sloan Foundation Fellow 1987-1989.

[1] (a) Parshall, G. W. *Organometallics* **1987**, *6*, 687-692. (b) Wynne, K. J.; Rice, R. W. *Annu. Rev. Mater. Sci.* **1984**, *14*, 297-334. (c) Rice, R. W. *Am. Ceram. Soc. Bull.* **1983**, *62*, 889-892. (d) Robinson, A. L. *Science* **1986**, *233*, 25-27. (e) *Transformation of Organometallics into Common and Exotic Materials: Design and Activation*; Laine, R. M., Ed.; NATO Advanced Science Institute Series; Martinus Nijhoff: Dordrecht, Holland, 1988. (f) *Ultrastructure Processing of Ceramics, Glasses and Composites*; Hench, L. L., Ulrich, D. R., Eds.; John Wiley & Sons: New York, 1983. (g) *Better Ceramics through Chemistry*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; North-Holland: New York, 1984.

[2] (a) Martin, M. J.; Qiang, G.-H.; Schleich, D. M. *Inorg. Chem.* **1988**, *27*, 2804-2808. (b) Czekaj, C. L.; Rau, M. S.; Geoffroy, G. L.; Guiton, T. A.; Pantano, C. G. *Ibid.* **1988**, *27*, 3267-3269. (c) Czekaj, C. L.; Geoffroy, G. L. *Ibid.* **1988**, *27*, 8-10.

[3] Steigerwald, M. L.; Rice, C. E. *J. Am. Chem. Soc.* **1988**, *110*, 4228-4231.

[4] (a) Brown, G. M.; Maya, L. *J. Am. Ceram. Soc.* **1988**, *80*, 78-82. (b) Maya, L. *Inorg. Chem.* **1987**, *26*, 1459-1462. (c) Maya, L. *Ibid.* **1986**, *25*, 4213-4217. (d) Bradley, D. C.; Hursthouse, M. B.; Abdul Malik, K. M.; Nielson, A. J.; Chota Vuru, G. B. *J. Chem. Soc., Dalton Trans.* **1984**, 1069-1075. (e) Seyferth, D.; Mignani, G. *J. Mater. Sci. Lett.* **1988**, *7*, 487.

0002-7863/90/1512-7989$02.50/0