Articles

Synthesis of Bimetallic Complexes via 4-Stannatetrahydro-*s*-indacenes

Ilya E. Nifant'ev,* Maxim V. Borzov, and Andrey V. Churakov

Department of Chemistry, Moscow University, Moscow 119899, Russia

Shaen G. Mkoyan and Lev O. Atovmyan

Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region 142432, Russia

4-Stanna-8-silatetrahydro-4,4,8,8-tetramethyl-*s*-indacene (4) reacts with $CpTiCl_3$ and $CpZrCl_3 \cdot 2THF$ in toluene (ratio 1:1) to give monotransmetallated products $CpMCl_2$ (η^5-$C_5H_4SiMe_2C_5H_4SnMe_2Cl$) (M = Ti (5), Zr (6)) in high yields. These compounds can be transformed into heteronuclear complexes of type L_nMCp–$SiMe_2$–$CpM'L'_m$ ($ML_n = TiCl_2Cp$, $M'L'_m = Rh(COD)$, 10; $ML_n = ZrCl_2Cp$, $M'L'_m = Rh(COD)$, 11; $ML_n = ZrCl_2Cp$, $M'L'_m = TiCl_2Cp$, 12; $ML_n = ZrCl_2Cp$, $M'L'_m = ZrCl_2Cp*$, 13) in reactions with $[Rh(COD)Cl]_2$, $CpTiCl_3$, and $Cp*ZrCl_3$, respectively. Compound 4 and its heteroanalog 4-stannatetrahydro-4,4,8,8-tetramethyl-*s*-indacene (14) react with $CpTiCl_3$ (ratio 1:2) and $(Cl_3TiCp)_2SiMe_2$ (16) (ratio 1:1) to give the corresponding monobridged $[CpTiCl_2(\eta^5$-$C_5H_4)]_2XMe_2$ (X = C (15), Si (8)) and doubly-bridged $(\eta^5:\eta^5$-$C_5H_4SiMe_2C_5H_4)(\eta^5:\eta^5$-$C_5H_4XMe_2C_5H_4)(TiCl_2)_2$ (X = C (17), Si (18)) Ti(IV) derivatives. They may be reduced by powdered zinc in toluene to the corresponding Ti(III) complexes, $[CpTiCl(\eta^5$-$C_5H_4)]_2XMe_2$ (X = C (20), Si (21)) and $(\eta^5:\eta^5$-$C_5H_4SiMe_2C_5H_4)(\eta^5:\eta^5$-$C_5H_4XMe_2C_5H_4)(TiCl)_2$ (X = C (22), Si (23)). Crystals of 23 are monoclinic, space group $P2_1/a$ with unit cell dimensions a = 16.033 (3) Å, b = 18.859 (4) Å, c = 7.997 (2) Å, γ = 96.82 (2)°, and Z = 4.

Introduction

Bimetallic compounds 1 containing two transition metal moieties joined to a bidentate biscyclopentadienyl ligand,
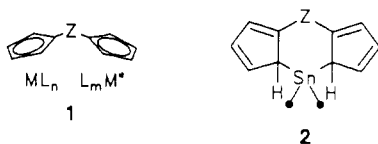
Cp-Z-Cp (Z = CR_2, SiR_2, etc), are considered as models for the study of the cooperative action of two metal centers toward various substrates. Numerous homometallic complexes 1a of this type have been synthesized and investigated.[1] However, the scope of the synthetic application to heterometallic compound 1b[2] synthesis is limited because general approaches have not been elaborated.

Recently, we have isolated 4-stannatetrahydro-*s*-indacenes 2,[3] which, in fact, are intramolecularly distannylated biscyclopentadienes Cp-Z-Cp (Z = CH_2, CMe_2, $SiMe_2$). Because their simple analogs trialkylstannylcyclopentadienes, $CpSnR_3$ (R = alkyl), are valuable precursors of η^5-cyclopentadienyl complexes of transition metals,[4] we supposed that 4-stannatetrahydro-*s*-indacenes 2 might be successfully applied in the synthesis of both homo- and heterodinuclear transition metal complexes of the type 1 as shown in Scheme I[5] (black dots on Sn represent methyl groups).

We have examined this possibility using 4,4,8,8-tetramethyl-8-sila-4-stannatetrahydro-*s*-indacene (4)[3a] (Z = $SiMe_2$ in 2) as the starting material for the preparation of novel homo- and heteronuclear bimetallic complexes 1, containing titanocene dichloride and zirconocene dichloride fragments ($ML_n = CpTiCl_2$, $CpZrCl_2$ in 1).

Results and Discussion

We investigated the reaction between 4 and the cyclopentadienyl trichlorides of titanium and zirconium (molar ratio 1:1) in THF and toluene. It was found that selective
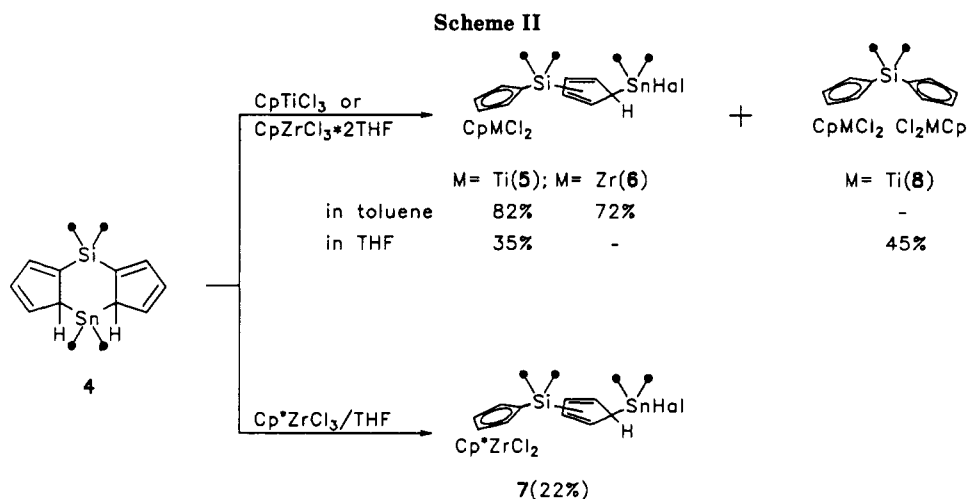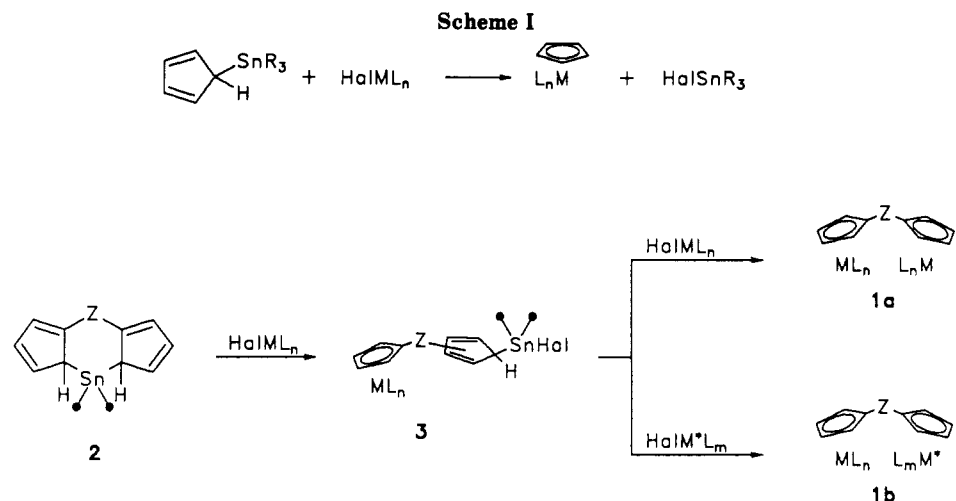
(1) (a) Wright, M. E.; Day, V. W. *J. Organomet. Chem.* 1987, *239*, 43. (b) LoSterzo, C.; Miller, M. M.; Stille, J. K. *Organometallics* 1989, *8*, 2331. (c) Janda, K. D.; McConnell, W. W.; Nelson, G. O.; Wright, M. E. *J. Organomet. Chem.* 1983, *259*, 139. (d) Wegner, P. A.; Uski, V. A. *Inorg. Chem.* 1979, *18*, 646. (e) Abriel, W.; Baum, G.; Heck, J.; Kriebisch, K.-A. *Chem. Ber.* 1990, *123*, 1763. (f) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* 1990, *112*, 9558. (g) Baumann, R.; Malisch, W. *J. Organomet. Chem.* 1986, *303*, C33. (h) Reddy, K. P.; Petersen, J. L. *Organometallics* 1989, *8*, 2107. (i) Schore, N. E.; Ilenda, C. S.; White, M. A.; Bryndza, H. E.; Matturro, M. G.; Bergman, R. G. *J. Am. Chem. Soc.* 1984, *106*, 7451. (j) Qiao, K.; Fischer, R. D.; Paolucci, G.; Traldi, P.; Celon, E. *Organometallics* 1990, *9*, 1361. (k) Bitterwolf, T. E.; Gambaro, A.; Gottardi, F.; Valle, G. *Organometallics* 1991, *10*, 1416 and references therein.

(2) (a) Buzinkai, J. F.; Schrock, R. R. *Organometallics* 1987, *6*, 1447. (b) Haerter, P.; Boguth, G.; Herdtweck, E.; Riede, J. *Angew. Chem.* 1989, *101*, 1058. (c) Schneider, P.; Werner, H. *J. Organomet. Chem.* 1990, *384*, C33. (d) LoSterzo, C. *Organometallics* 1990, *9*, 3185. (e) LoSterzo, C.; Stille, J. K. *Organometallics* 1990, *9*, 687. (f) Rausch, M. D.; Wang, Y.-P. *Organometallics* 1991, *10*, 1438 and references therein.

(3) (a) Nifant'ev, I. E.; Chestakova, A. K.; Lemenovskii, D. A.; Slovokhotov, Yu. L.; Struchkov, Yu. T. *Metalloorg. Khim.* 1991, *10*, 293. (b) Nifant'ev, I. E.; Yarnikh, V. L.; Borzov, M. V.; Mazurchik, B. A.; Rozniatovskii, V. A.; Mstislavskii, V. I.; Ustynyuk, Yu. A. *Organometallics* 1991, *10*, 3739.

(4) (a) Burt, R. J.; Chatt, J.; Leigh, G. J.; Teuben, J. H.; Westerhof, A. *J. Organomet. Chem.* 1977, *129*, C33. (b) Jutzi, P.; Kuhn, M. *J. Organomet. Chem.* 1979, *173*, 221. (c) Hubert-Pfalzgraf, L. G.; Riess, J. G. *Inorg. Chim. Acta* 1981, *52*, 231. (d) Beachley, O. T.; Less, J. F.; Glassman, T. E.; Churchill, M. R.; Buttrey, L. A. *Organometallics* 1990, *9*, 2488.

(5) Nifant'ev, I. E.; Borzov, M. V.; Ivchenko, P. V.; Yarnykh, V. L.; Ustynyuk, Yu. A. *Organometallics* 1992, *11*, 3462.

Scheme I

Scheme II

	CpTiCl₃ or			M= Ti(8)
		M= Ti(5); M= Zr(6)		
	in toluene	82%	72%	-
	in THF	35%	-	45%

7(22%)

monotransmetallation occurred when the reaction was carried out in toluene. A monotitanium product **5** (82%) was formed at rt (room temperature), and its zirconium analog **6** (72%) was formed at 90 °C. When THF was used as solvent, the yields of the desired compounds were lower. Thus compound **5** was formed in 35% yield, while the dititanium complex **8** (45%) was the main product. In the attempted reaction between **4** and CpZrCl₃·2THF, no products were observed and the initial zirconium complex was recovered almost completely (Scheme II).

Two general solvent factors may be responsible for the observed phenomena. The first of them is connected with the difference of the solvation energy of Me₂SnCl₂ in THF and in toluene. It is obvious that the elimination of Me₂SnCl₂ in the second step of transmetalation should be more preferred in ethers than in aromatic solvents.[6] Therefore, the yield of **5** in THF is smaller than in toluene. Second, CpZrCl₃ becomes coated in THF media owing to the formation of a stable adduct CpZrCl₃·2THF. When CpZrCl₃·2THF and **4** react in toluene, heating is necessary in order to decompose the zirconium solvate. The intermediate CpZrCl₃ is observed as a thin white precipitate which dissolves completely by the end of the reaction. In contrast, the reaction of **4** with Cp*ZrCl₃ (Cp* = C₅Me₅), which does not form a stable adduct with THF, proceeds relatively easily in THF and the monozirconium complex **7** was isolated. The isolated yield of **7** was not high owing to its significant solubility even in pentane.

Monotransmetalated compounds **5–7** are temperature unstable complexes. Besides bimetallic derivatives there are ansa compounds as byproducts in the reaction of
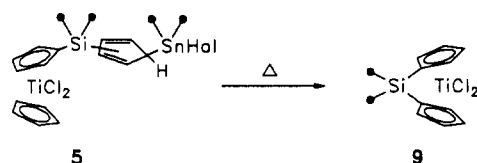
monotransmetalation. Heating **5** in toluene for several hours gives 1,1′-dimethylsilylenetitanocene dichloride (**9**).[7] The same product is formed when a solution of **5** in toluene is allowed to stand at rt for 1 month. A similar process takes place in the case of **6**, but the rate of decomposition of the zirconium derivative under the same conditions is much slower than that of the titanium complex.

The monotransmetalated products **5** and **6** can be easily converted to heterobinuclear biscyclopentadienyl complexes. Thus, **5** and **6** give **10** and **11** (Scheme III) when treated with [Rh(COD)Cl]₂ in THF, while **6** gives zirconium–titanium **12** and nonsymmetrical zirconium–zirconium **13** complexes when treated in THF with CpTiCl₃ and Cp*ZrCl₃, respectively. One should take into account the great significance of the sequence of inserting organometallic fragments. As the monotransmetalated compounds **5** and **6** are thermally unstable, the less reactive metal halide must be chosen first to react with **4**. For

---

(6) *Comprehensive Organic Chemistry*; v.3: Barton, P. Ollis, W. D., Eds.; Pergamon Press: London, 1979; Vol. 3.

(7) (a) Kopf, H.; Klouras, N. *Z. Naturforsch, B* **1983**, *38B*, 321. (b) Bajgur, C. S.; Tikkanen, W. R.; Petersen, J. L. *Inorg. Chem.* **1985**, *24*, 2539.

Table I. Important Geometric Characteristics of 23 Compared with Those of Similar Molecules

	M–M (Å)	M–Cl(H) (Å)	M–L–M* (deg)	L–M–L* (deg)	M–C(Cp) (Å)	ref
23	3.65	2.51	93.5	86.5	2.39	a
[(CH$_3$)$_2$Si(C$_5$H$_4$)$_2$]$_2$Yb$_2$Cl$_2$	3.75		90.8	89.3		9
[(C$_5$H$_5$)$_2$TiCl]$_2$	3.95	2.54	102.0	78.0	2.38	10
(C$_5$H$_5$)$_2$Ti$_2$(C$_{10}$H$_8$)Cl$_2$	3.64	2.57	92.5	81.5	2.38	11
(C$_5$H$_5$)$_2$Ti$_2$(C$_{10}$H$_8$)(H)Cl	3.13	2.49 (2.17)	77.6 (93.0)	92.0	2.35	12
[Me$_4$C$_5$(C$_5$H$_4$)SiEt$_2$]$_2$Lu$_2$H$_2$	3.39	(2.14)	105.0	75.0	2.68	1j

a This work.

Scheme III

Scheme IV

Scheme V
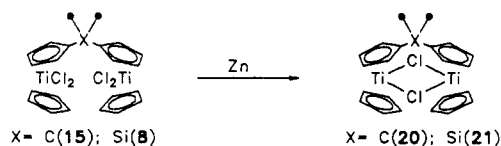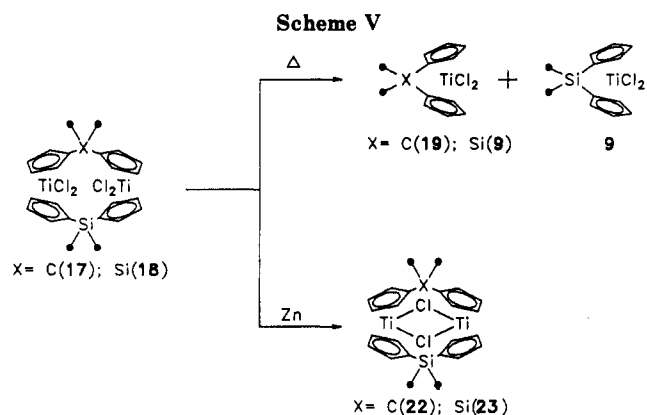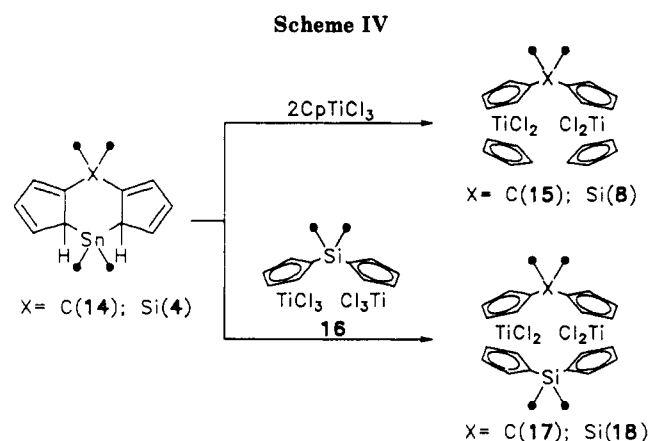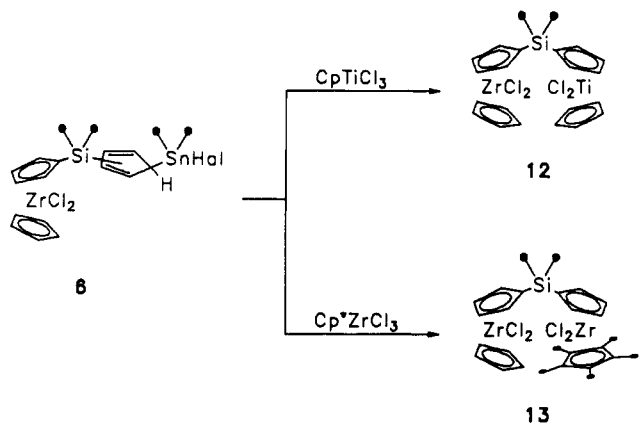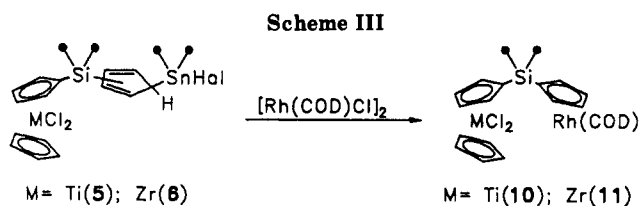
instance, **12** was not formed if **5** was treated with CpZrCl$_3$·2THF in toluene. In this reaction ansa compound **9** was isolated.

Unfortunately, there are no detailed data on mechanisms of transmetalation reactions of stannylated cyclopentadienes by metal halides. Therefore, the reactivities of different metal halides toward stannylated cyclopentadienes have not been compared. As for the transition metal reagents we used, their reactivity decreases from [Rh(COD)Cl]$_2$ in CpZrCl$_3$·2THF as

[Rh(COD)Cl]$_2$ > CpTiCl$_3$ > Cp*ZrCl$_3$ >

CpZrCl$_3$·2THF
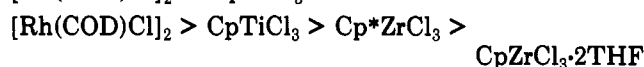
both in toluene and in THF.

As mentioned above, dititanium complex **8** was isolated as a byproduct of the reaction between **4** and CpTiCl$_3$ (molar ratio 1:1) in THF. When **4** was treated with 2 equiv of CpTiCl$_3$, **8** was obtained in almost quantitative yield. The similar dititanium compound **15** could be prepared from 4-stanna-3a,4,4a,8-tetrahydro-4,4,8,8-tetramethyl-*s*-indacene[3b] (**14**) (Scheme IV). If dititanium complex (Cl$_3$TiC$_5$H$_4$)$_2$SiMe$_2$ (**16**)[8] was used instead of CpTiCl$_3$, the corresponding complexes **17** and **18** were isolated. Unfortunately, complexes **17** and **18** are insoluble in all available solvents and, moreover, thermally unstable. Thus, when **17** and **18** were heated in high vacuum, a mixture of ansa compounds sublimed. The same decomposition occurred when they were heated in THF for several hours. To prove the structure of monobridged (**8** and **15**) and doubly-bridged (**17** and **18**) dititanium com-

plexes, we isolated and investigated their reduced forms **20–23**. The reduction of these dititanium compounds proceeded almost quantitatively, and finely crystallizing dititanium complexes were isolated (Scheme V). All of them are soluble in THF and aromatic solvents and were characterized mass spectroscopically. Their mass spectra showed the molecular ion peak in contrast to their dititanium precursors. The structure of **23** was established by means of X-ray analysis.

X-ray Analysis of 23. The structural investigation revealed two independent molecules each containing a crystallographically imposed center of symmetry. The structure of the molecule is presented in the Figure 1 and in general is very similar to that of its Yb counterpart [(CH$_3$)$_2$Si(C$_5$H$_4$)$_2$]$_2$Yb$_2$Cl$_2$ (**24**).[9] The M···M* distances are

(8) Nifant'ev, I. E.; Butakov, K. A.; Aliev, Z. G.; Urazowskii, I. F. *Metalloorg. Khim.* **1991**, *4*, 1265.

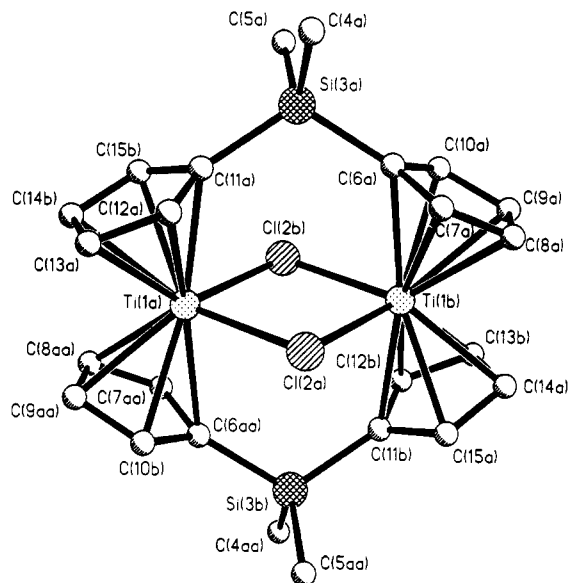(9) Hock, N.; Oroschin, W.; Paolucci, G.; Fischer, R. D. *Angew. Chem.* **1986**, *98*, 748.

Figure 1. Molecular structure of **23**.

Table II. Crystal and Intensity Data for the X-ray Diffraction Study of 23

molecular formula	$C_{24}H_{28}Si_2Cl_2Ti_2$
cryst system	monoclinic
space group	$P2_1/a$ (No. 14)
a	16.033 (3) Å
b	18.859 (4) Å
c	7.997 (2) Å
γ	96.82 (2)°
V	2400.8 (4) Å³
z	4
ρ(calcd)	1.504 g/cm³
ρ(measd)	1.51 g/cm³
abs coeff	9.74 cm⁻¹
T	22 (2) °C
diffractometer	KUMA diffraction KM-4
radiation (λ)	Mo Kα (0.710 73 Å)
monochromator	graphite crystal
scan type	θ–2θ
scan speed	variable
takeoff angle	3.5
data limits	$4.0 \leq 2\theta \leq 52.0$
reflcns measd	$\pm h, +k, +l$
no. of unique data	4197
no. of nonzero data	3549 ($I \geq 3\sigma(I)$)
R	2.8%
R_w	2.8%

3.65 and 3.75 Å in **23** and **24**. The Cl–M–Cl* and M–Cl–M* angles are 86.5 and 93.5° in **23** and 89.3 and 90.8° in **24**, respectively. The (Cp)C–Si–C(Cp') angles are 115.7 and 118.7°. The former value is nearer to the ideal tetrahedral angle of 109.5°, which may be due to relief of the strain of the chelating $(CH_3)_2Si(C_5H_4)_2$ in **23** as compared with **24**. The average values of the Si–CH₃ and Si–C(Cp) bond lengths of 1.86 and 1.87 Å in **23** are also indicative of the absence of any significant strain in this ligand. In Table I, important geometric characteristics of **23** are compared with the corresponding values of **24** and the other close analogs. As is evident from these data, only $(C_5H_5)_2Ti_2(C_{10}H_8)Cl_2$ contains a Ti₂Cl₂ fragment, which is similar from the structural point of view to that of **23**. It is noteworthy that $(C_5H_5)_2Ti_2(C_{10}H_8)Cl_2$, like $[(CH_3)_2Si(C_5H_4)_2]_2Yb_2Cl_2$, can be obtained in a one-step reaction from a mononuclear precursor,[9,11] which may be regarded

Table III. Atomic Positional Parameters for 23

atom	x/a	y/b	z/c
Ti1A	0.9209 (0)	0.5574 (0)	0.0593 (1)
Cl2A	1.0674 (1)	0.5408 (1)	0.1473 (2)
Si3A	0.9016 (1)	0.3682 (1)	0.2292 (2)
C4A	0.9056 (4)	0.3385 (3)	0.4509 (6)
C5A	0.8219 (3)	0.3084 (3)	0.1102 (7)
C6A	0.8685 (3)	0.4598 (2)	0.2337 (5)
C7A	0.8986 (3)	0.5163 (2)	0.3431 (5)
C8A	0.8523 (3)	0.5735 (3)	0.3219 (6)
C9A	0.7898 (3)	0.5536 (3)	0.2019 (6)
C10A	0.7992 (3)	0.4847 (3)	0.1476 (6)
C11A	1.0058 (3)	0.3606 (2)	0.1309 (6)
C12A	1.0860 (3)	0.3803 (3)	0.2016 (6)
C13A	1.1475 (3)	0.3578 (3)	0.0995 (6)
C14A	0.8924 (3)	0.6788 (3)	0.0371 (6)
C15A	0.9797 (3)	0.6767 (2)	0.0193 (6)
Ti1B	0.5632 (1)	0.0795 (0)	0.0805 (1)
Cl2B	0.4427 (1)	−0.0070 (1)	0.1827 (1)
Si3B	0.6143 (1)	−0.1024 (1)	0.2229 (2)
C4B	0.5715 (3)	−0.1226 (3)	0.4364 (6)
C5B	0.7108 (3)	−0.1461 (3)	0.1848 (6)
C6B	0.6441 (3)	−0.0045 (2)	0.2080 (5)
C7B	0.6983 (3)	0.0342 (3)	0.0887 (6)
C8B	0.7111 (3)	0.1058 (3)	0.1344 (6)
C9B	0.6683 (3)	0.1143 (3)	0.2849 (6)
C10B	0.6271 (3)	0.0472 (3)	0.3311 (6)
C11B	0.5344 (3)	−0.1417 (2)	0.0693 (6)
C12B	0.4519 (3)	−0.1742 (2)	0.1067 (6)
C13B	0.5842 (3)	0.2060 (3)	0.0391 (6)
C14B	0.5260 (4)	0.1933 (3)	0.1703 (6)
C15B	0.4525 (3)	0.1550 (3)	0.1047 (6)

Table IV. Bond Distances (Å) in $C_{24}H_{28}Si_2Cl_2Ti_2$

	molecule A	molecule B
Ti1⋯Ti1'	3.650 (0)	3.648 (1)
Ti1–Cl2	2.507 (2)	2.513 (2)
Ti1–Cl2'	2.505 (2)	2.505 (1)
Ti1–C6	2.382 (4)	2.391 (4)
Ti1–C7	2.411 (4)	2.422 (5)
Ti1–C8	2.407 (5)	2.403 (5)
Ti1–C9	2.385 (5)	2.383 (5)
Ti1–C10	2.356 (5)	2.363 (5)
Ti1–C11'	2.378 (4)	2.386 (5)
Ti1–C12'	2.403 (5)	2.365 (4)
Ti1–C13'	2.406 (5)	2.392 (6)
Ti1–C14'	2.394 (6)	2.404 (6)
Ti1–C15'	2.356 (4)	2.411 (5)
Si3–C4	1.863 (5)	1.863 (5)
Si3–C5	1.862 (6)	1.863 (5)
Si3–C6	1.867 (4)	1.855 (4)
Si3–C11	1.868 (5)	1.863 (5)
C6–C7	1.418 (6)	1.431 (7)
C7–C8	1.390 (7)	1.390 (8)
C8–C9	1.406 (7)	1.404 (7)
C9–C10	1.395 (8)	1.406 (8)
C6–C10	1.433 (7)	1.434 (7)
C11–C12	1.413 (7)	1.422 (7)
C12–C13	1.385 (7)	1.404 (7)
C13–C14	1.405 (7)	1.406 (7)
C14–C15	1.412 (7)	1.408 (8)
C11–C15	1.425 (6)	1.434 (7)

as an evidence for its relative stability. One can deduce that $[(CH_3)_2Si(C_5H_4)_2]_2Ti_2Cl_2$, although synthesized in a more sophisticated way, also is a relatively stable molecule, at least in terms of the absence of intramolecular strain.

Experimental Section

(10) Jungst, R.; Secutowski, D.; Davis, J.; Luly, M.; Stucky, G. *Inorg. Chem.* **1977**, *16*, 1645.

(11) Olthof, G. J. *J. Organomet. Chem.* **1977**, *128*, 367.

(12) Perevalova, E. G.; Urazowskii, I. F.; Lemenovskii, D. A.; Slovokhotov, Yu. L.; Struchkov, Yu. T. *J. Organomet. Chem.* **1985**, *289*, 319.

Table V. Bond Angles (deg) in $C_{24}H_{28}Si_2Cl_2Ti_2$

molecule A		molecule B	
Ti1–Cl2–Ti1'	93.49 (6)	Ti1–Cl2–Ti1'	93.27 (6)
Cl2–Ti1–Cl2'	86.51 (6)	Cl2–Ti1–Cl2'	86.73 (6)
C4–Si3–C5	110.5 (3)	C4–Si3–C5	111.4 (2)
C4–Si3–C6	106.5 (2)	C4–Si3–C6	107.9 (2)
C4–Si3–C11	108.4 (2)	C4–Si3–C11	107.7 (2)
C5–Si3–C6	108.7 (2)	C5–Si3–C6	107.5 (2)
C5–Si3–C11	107.1 (2)	C5–Si3–C11	106.5 (2)
C6–Si3–C11	115.7 (2)	C6–Si3–C11	115.9 (2)
C6–C7–C8	110.0 (4)	C6–C7–C8	109.3 (4)
C6–C10–C9	109.2 (4)	C6–C10–C9	108.9 (4)
C7–C8–C9	107.8 (4)	C7–C8–C9	108.6 (5)
C8–C9–C10	108.0 (5)	C8–C9–C10	107.8 (5)
C7–C6–C10	104.9 (4)	C7–C6–C10	105.3 (4)
C11–C12–C13	110.0 (4)	C11–C12–C13	108.9 (4)
C12–C11–C15	105.7 (4)	C12–C11–C15	106.1 (4)
C12–C13–C14	108.0 (5)	C12–C13–C14	108.4 (5)
C13–C14–C15	107.6 (4)	C13–C14–C15	107.9 (5)
C11–C15–C14	108.6 (4)	C11–C15–C14	108.7 (4)

Elemental analyses were performed in the analytical laboratory of Moscow University. The conditions of the X-ray experiment and positional parameters of **23** are given in Tables II and III. All hydrogen atom coordinates found from the Fourier differential map and refined in isotropic approximation. Important bond distances and angles are given in Tables IV and V.

Preparation of 4 (Improved Procedure). A cooled (–30 °C) solution of 59.54 g (316 mmol) of $(C_5H_5)_2SiMe_2$[7a] in 600 mL of dry Et_2O was treated under static argon with 283 mL of 2.23 N n-BuLi solution in hexane within 1.5 h, and the resultant mixture was allowed to warm to rt. Then 69.45 g (316 mmol) of Me_2SnCl_2 in 700 mL of Et_2O was added within 0.5 h, and the mixture was stirred and refluxed for 15 h. The yellowish solution was decanted from a white precipitate, evaporated in vacuo, and distilled twice. Bp: 112 °C/10^{-2} Torr. A 57.59-g yield (54%) of **4** was isolated. The ¹H NMR spectrum of **4** thus prepared is identical to that observed earlier.[3a]

Preparation of 14. **14** was obtained (like **4**) from 68.05 g (395 mmol) and $(C_5H_5)_2CMe_2$,[3b] 326 mL of 2.45 N n-BuLi in hexane, and 87.0 g (395 mmol) of Me_2SnCl_2. Bp: 107–110 °C/5 × 10^{-2} Torr. A 68.2-g yield (54%) of **14** was isolated. The ¹H NMR spectrum of **14** thus prepared is identical to that observed earlier.[3b]

Preparation of 5. A 0.620-g amount (2.86 mmol) of CpTiCl₃ and 7.23 mL of a 0.396 M solution of **4** in toluene were mixed in 40 mL of toluene at rt and left to stand for 3 days. The components soluble in toluene were transferred into another flask, and the solvent was removed. The crystalline product remaining was washed with pentane and dried in vacuo to give 1.302 g (2.35 mmol, 82.1%) of the desired monotransmetalated compound **5**. ¹H NMR (toluene-d_8, 30 °C): δ 6.58 (m, C_5H_4 stannylated ring, 2H), 6.42 (m, C_5H_4 stannylated ring, 2H), 6.38 (t, C_5H_4 titanocene fragment, 2H), 5.94 (s, C_5H_5, 5H), 5.77 (t, C_5H_4 titanocene fragment, 2H), 0.64 (s, $(CH_3)_2Si$, 6H), 0.05 (s, $(CH_3)_2SnCl$, $^2J_{^1H-^{119}Sn}$ = 59.2 Hz, 6H). Anal. Calcd for $C_{19}H_{25}Cl_3SiSnTi$: C, 41.16; H, 4.55. Found: C, 41.51; H, 4.38.

Preparation of 6. A suspension of 2.12 g (5.20 mmol) of CpZrCl₃·2THF in 40 mL of toluene was treated with 13.1 mL of a 0.396 M solution of **4** in toluene at 90–100 °C during 1 h with vigorous stirring. A thin white crystalline precipitate appeared and dissolved gradually. Removal of the toluene and washing of the residue with pentane gave a white residue, which was dried in vacuo to give 2.24 g (3.75 mmol, 72%) of **6**. ¹H NMR (toluene-d_8, 30 °C): δ 6.60 (m, C_5H_4 stannylated ring, 2H), 6.40 (m, C_5H_4 stannylated ring, 2H), 6.35 (t, C_5H_4 zirconocene fragment, 2H), 5.91 (s, C_5H_5, 5H), 5.84 (t, C_5H_4 zirconocene fragment, 2H), 0.58 (s, $(CH_3)_2Si$, 6H), 0.01 (s, $(CH_3)_2SnCl$, $^2J_{^1H-^{119}Sn}$ = 59.2 Hz, 6H). Anal. Calcd for $C_{19}H_{25}Cl_3SiSnZr$: C, 38.18; H, 4.22. Found: C, 38.23; H, 4.07.

Preparation of 7. A mixture of 1.15 g (3.46 mmol) of Cp*ZrCl₃ and 1.43 g (4.28 mmol) of **4** in 40 mL of THF was kept at rt for 12 h. The solvent was removed, and the mixture was extracted with toluene. On evaporation of the toluene, a yellowish crystalline precipitate formed. It was washed with pentane and dried in vacuo to give 0.51 g (0.76 mmol, 22%) of **7**. ¹H NMR (THF-d_8, 30 °C): δ 6.71 (m, C_5H_4 stannylated ring, 2H), 6.61 (m, C_5H_4 stannylated

ring, 2H), 6.50 (t, C_5H_4 zirconocene fragment, 2H), 6.21 (t, C_5H_4 zirconocene fragment, 2H), 2.00 (s, $C_5(CH_3)_5$, 15H), 0.47 (s, $(CH_3)_2Si$, 6H), 0.18 (s, $(CH_3)_2SnCl$, $^2J_{^1H-^{119}Sn}$ = 62.8 Hz). Anal. Calcd for $C_{24}H_{35}Cl_3SiSnZr$: C, 43.16; H, 5.28. Found: C, 43.32; H, 5.19.

Preparation of 10. A mixture of 0.61 g (0.96 mmol) of **5** and 0.24 g (0.48 mmol) of [(COD)RhCl]₂ in 10 mL of THF was stirred for 10 h at rt. After removal of the THF, the violet precipitate was washed with ether and dried in vacuo. Violet crystalline product **10** (0.51 mmol, 53%) was obtained. ¹H NMR (CDCl₃, 30 °C): δ 6.93 (t, C_5H_4 titanocene fragment, 2H), 6.56 (t, C_5H_4 titanocene fragment, 2H), 6.37 (s, C_5H_5, 5H), 5.50 (t, C_5H_4–rhodium fragment, 2H), 4.74 (t, C_5H_4 rhodium fragment, 2H), 3.90 (br s, COD vinylic, 4H), 2.15 (m, COD allylic, 4H), 1.89 (m, COD allylic, 4H), 0.56 (s, $(CH_3)_2Si$, 6H). Anal. Calcd for $C_{25}H_{31}Cl_2RhSiTi$: C, 51.66; H, 5.38. Found: C, 51.12; H, 5.17.

Preparation of 11. A mixture of 0.74 g (1.24 mmol) of **6** and 0.31 g (0.62 mmol) of [(COD)RhCl]₂ in 15 mL of THF was kept at rt during 12 h. The solvent was removed, and the yellow crystals remaining were washed with pentane and dried in vacuo to give 0.54 g (0.87 mmol, 70%) of **14**. ¹H NMR (THF-d_8, 30 °C): δ 6.70, 6.58 (all t, C_5H_4 zirconocene fragment, 2H), 5.43, 4.77 (all t, C_5H_4 rhodium fragment, 2H), 3.88 (br s, COD vinylic, 4H), 2.07 (m, COD allylic, 4H), 0.53 (s, $(CH_3)_2Si$, 6H). Anal. Calcd for $C_{25}H_{31}Cl_2RhSiZr$: C, 48.07; H, 5.00. Found: C, 47.89; H, 4.83.

Preparation of 12. A solution of 0.28 g (0.48 mmol) of **6** and 0.10 g (0.48 mmol) of CpTiCl₃ in 7 mL of THF was left at 25 °C for 20 h. After removal of the THF, the residue was recrystallized from toluene to give 0.14 g (0.24 mmol, 50%) of red crystals of **12**. ¹H NMR (THF-d_8, 30 °C): δ 6.82, 6.75, 6.65, 6.62 (all t, C_5H_4, 2H), 6.49, 6.43 (all s, C_5H_5, 5H), 0.65 (s, $(CH_3)_2Si$, 6H). Anal. Calcd for $C_{22}H_{24}Cl_4SiTiZr$: C, 44.23; H, 4.05. Found: C, 43.97; H, 3.86.

Preparation of 13. A solution of 0.90 g (1.50 mmol) of **6** and 0.50 g (1.50 mmol) of Cp*ZrCl₃ in THF was left for 1 week at rt. The solvent was evaporated, and the resulting yellow oil was dissolved in toluene. Within 1 day a white thin crystalline precipitate began to form. In 1 week the precipitate was separated and recrystallized from THF, washed with pentane, and dried in vacuo to give 0.24 g (22%) of **13**. ¹H NMR (THF-d_8, 30 °C): δ 6.71, 6.56, 6.53, 6.24 (all t, C_5H_4, all 2H), 6.36 (s, C_5H_5, 5H), 2.01 (s, $C_5(CH_3)_5$, 15H), 0.65 (s, $(CH_3)_2Si$, 6H). Anal. Calcd for $C_{27}H_{34}Cl_4SiZr_2$: C, 45.62; H, 4.82. Found: C, 45.35; H, 4.87.

Preparation of 8. A solution of 3.0 g (9.0 mmol) of **4** and 3.9 g (18 mmol) of CpTiCl₃ in 70 mL of THF was left for 10 h. The precipitate which resulted was washed twice with THF (50 mL) and then with ether. The crystalline residue was dried in vacuo to give 4.0 g (81%) of **8**. ¹H NMR (THF-d_8): δ 6.84, 6.65 (all t, C_5H_4, all 2H), 6.51 (s, C_5H_5, 5H), 0.64 (s, $(CH_3)_2Si$, 6H). Anal. Calcd for $C_{22}H_{24}Cl_4SiTi_2$: C, 47.69; H, 4.37. Found: C, 47.80; H, 4.44.

Preparation of 15. The reaction was performed in a manner analogous to that for **8**. The initial indacene **14** was used instead of **4**. The yield of **15** was 89%. Anal. Calcd for $C_{23}H_{24}Cl_4Ti_2$: C, 51.34; H, 4.50. Found: C, 51.60; H, 4.29.

Preparation of 17 and 18. The reaction was performed in a manner analogous to that for **8**. $(Cl_3TiCp)_2SiMe_2$[8] was used instead of CpTiCl₃. (Note that the temperature of the reaction mixture cannot be higher than 20–30 °C). The yield of **17** was 22%. Anal. Calcd for $C_{25}H_{28}Cl_4SiTi_2$: C, 50.54; H, 4.75. Found: C, 50.53; H, 4.63. The yield of **18** was 16%. Anal. Calcd for $C_{24}H_{28}Cl_4Si_2Ti_2$: C, 47.24; H, 4.63. Found: C, 47.08; H, 4.50.

Thermolysis of 17 and 18. A small amount of **17** was placed in a evacuated sublimation apparatus and heated carefully with a Bunsen burner flame. A beautifully crystalline, red solid began to sublime at once. The decomposition of **17** left no residue and formed an equimolar mixture of the two known[7,8] ansa compounds **9** and **19**, which were identified by NMR. The sublimation of **18** led only to **9**.

Reduction of Dititanium(IV) Derivatives. A suspension of 0.5 mmol of the corresponding dititanium(IV) derivative and 0.2 g of zinc powder in 10 mL of toluene was stirred vigorously at 20 °C until the starting compound dissolved. The brown solution was decanted from residual zinc, and the solvent was removed. Recrystallization from ether or THF gave 0.20 g (84%) of **20**, 0.19 g (78%) of **21**, 0.20 g (75%) of **22**, and 0.19 g (71%) of **23**. Anal. Calcd for $C_{23}H_{24}Cl_2Ti_2$ (**20**): C, 59.14; H, 5.18. Found: C, 58.89; H, 4.93. Mass spectrum (m/z): M⁺, 466 (⁴⁸Ti, ³⁵Cl). Anal.

Calcd for $C_{22}H_{24}Cl_2Ti_2$ (21): C, 54.69; H, 5.01. Found: C, 54.33; H, 4.75. Mass spectrum (m/z): M+, 482 (48Ti, 35Cl). Anal. Calcd for $C_{25}H_{28}Cl_2SiTi_2$ (22): C, 57.39; H, 5.39. Found: C, 57.09; H, 5.43. Mass spectrum (m/z): M+, 522 (48Ti, 35Cl). Anal. Calcd for $C_{24}H_{28}Cl_2Si_2Ti_2$ (23): C, 53.45; H, 5.23. Found: C, 53.17; H, 5.09. Mass spectrum (m/z): M+, 538 (48Ti, 35Cl).

Enthalpies of Reaction of Cp*Ru(CH₃CN)₃⁺O₃SCF₃⁻ (Cp* = η⁵-C₅Me₅) with Arenes. Solution Thermochemical Study of Arene Binding to the Cp*Ru⁺ Fragment

Steven P. Nolan,* Kenneth L. Martin, and Edwin D. Stevens

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

Paul J. Fagan*

Central Research and Development Department, E. I. du Pont de Nemours & Co., Inc., Experimental Station, P.O. Box 80328, Wilmington, Delaware 19880-0328

Received July 1, 1992

The enthalpies of reaction of Cp*Ru(CH₃CN)₃OTf (Cp* = η⁵-C₅(CH₃)₅, OTf = O₃SCF₃) with a series of arenes have been measured by solution calorimetry. The results of this study are used to establish the following relative stability scale leading to the formation of Cp*Ru(arene)OTf complexes in THF (in kcal/mol): naphthalene, −1.7 ± 0.1; benzene, −3.4 ± 0.1; biphenyl, −3.6 ± 0.1; toluene, −4.3 ± 0.2; p-xylene, −4.6 ± 0.2; (trimethylsilyl)benzene, −5.0 ± 0.2; anisole, −5.4 ± 0.2; mesitylene, −5.5 ± 0.1; indole, −7.3 ± 0.2; N,N-dimethylaniline, −7.5 ± 0.1; p-bis(dimethylamino)benzene, −8.3 ± 0.2. The solid-state structure of one of these arene complexes, Cp*Ru[C₆H₅(Si(CH₃)₃)]OTf, was determined by a low-temperature data collection X-ray crystallographic study. This investigation illustrates the presence of steric interactions between the phenyl TMS methyl groups and the Cp* methyl group and explains the small measured enthalpy of reaction. The enthalpies of arene substitution from Cp*Ru(CH₃CN)₃OTf span some 6.6 kcal/mol and vary as a function of the electron-donating ability of the arene. Factors affecting the Ru–arene bond energy are discussed, and thermodynamic comparisons with other organometallic systems are presented.

Introduction

A better knowledge of metal–ligand bond energies is vital to a complete understanding of the driving forces behind important organotransition-metal-mediated reactions. A variety of methods have been used to obtain metal–ligand bond disruption enthalpies for organometallic systems.[1-3] These include kinetic,[2c,h,4] photoacoustic,[2i,5] laser pyrolytic,[6] and one-[7,8] and two-electron-redox[2d,j,9] approaches. A thermochemical technique which has proven successful for a number of oganometallic systems is solution calorimetry. Some of these solution calorimetric studies have led to the determination of relative and absolute bond disruption enthalpies, the latter through an accessible thermodynamic anchor[7,10a] or estimation of a thermodynamic anchor point.[8-10] Even though the knowledge of absolute bond dissociation energies is fundamental to a complete understanding of a transition-metal system, as they allow direct thermodynamic comparison between different systems, relative bond disruption

(1) (a) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629–688. (b) Marks, T. J., Ed. Metal–Ligand Bonding Energetics in Organotransition Metal Compounds. *Polyhedron* **1988**, *7*. (c) Marks, T. J., Ed. *Bonding Energetics in Organometallic Compounds*; ACS Symposium Series 428; American Chemical Society: Worthington, DC, 1990. (d) Hoff, C. D. *Prog. Inorg. Chem.* **1992**, *40*, 503–561.

(2) For some leading references, see also: (a) Pilcher, G.; Skinner, H. H. In *The Chemistry of the Metal–Carbon Bond*; Harley, F. R., Patai, S., Eds.; Wiley: New York, 1982; pp 43–90. (b) Connor, J. A. *Top Curr. Chem.* **1977**, 71–110. (c) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238–244. (d) Mondal, J. U.; Blake, D. M. *Coord. Chem. Rev.* **1983**, *47*, 204–238. (e) Mansson, M. *Pure Appl. Chem.* **1983**, *55*, 417–426. (f) Skinner, H. A.; Connor, J. A. *Pure Appl. Chem.* **1985**, *57*, 79–88. (g) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41–59. (h) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41–48. (i) Nolan, S. P.; Hoff, C. D.; Stoutland, P. O.; Newman, L. J.; Buchanan, J. M.; Bergman, R. G.; Yang, G. K.; Peters, K. G. *J. Am. Chem. Soc.* **1987**, *109*, 3143–3145 and references therein. (j) Dias, A. R.; Salema, M. S.; Martinho-Simoes, J. A. *J. Organomet. Chem.* **1981**, *222*, 69–78.

(3) (a) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701–7715. (b) Dias, A. R.; Simoes, J. A. M. In ref 1b, pp 1531–1544. (c) Lappert, M. F.; Patil, D.; Pedley, J. B. *J. Chem. Soc., Chem. Commun.* **1975**, 830–831.

(4) (a) Halpern, J. In ref 1b, pp 1483–1490. (b) Hay, B. P.; Finke, R. G. In ref 1b, pp 1469–1481. (c) Koenig, T. W.; Hay, B. P.; Finke, R. G. In ref 1b, pp 1499–1516. (d) Wayland, B. B. In ref 1b, pp 1545–1455. (e) Geno, M. K.; Halpern, J. *J. Chem. Soc., Chem. Commun.* **1987**, 1052–1053.

(5) (a) Yang, G. K.; Vaida, V.; Peters, K. S. In ref 1b, pp 1619–1622. (b) Rothberg, L. J.; Simon, J. D.; Bernstein, M.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 3464–3470.

(6) Smith, G. P. In ref 1b, pp 1605–1608.

(7) (a) Nolan, S. P.; Stern, D. L.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844–7853. (b) Toscano, P. J.; Seligson, A. L.; Curran, M. T.; Skrobutt, A. T.; Sonnenberger, D. C. *Inorg. Chem.* **1989**, *28*, 166–168.

(8) (a) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824–6832. (b) Sonnenberger, D. C.; Morss, L. R.; Marks, T. J. *Organometallics* **1985**, *4*, 352–355. (c) Bruno, J. W.; Stecher, H. A.; Morss, L. R.; Sonnenberger, D. C.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7275–7280 and ref 4. (d) Nolan, S. P.; Stern, D. L.; Hedden, D.; Marks, T. J. In ref 1c, pp 159–174. (e) Nolan, S. P.; Porchia, M.; Marks, T. J. *Organometallics* **1991**, *10*, 1087–1090.

(9) Stoutland, P. O.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. In ref 1b, pp 1429–1440.

(10) (a) Nolan, S. P.; Lopez de la Vega, R.; Hoff, C. D. *Organometallics* **1986**, *5*, 2529–2537. (b) Nolan, S. P.; Hoff, C. D.; Landrum, J. T. *J. Organomet. Chem.* **1985**, *282*, 357–362. (c) Hoff, C. D.; Nolan, S. P. *J. Organomet. Chem.* **1985**, *290*, 365–373. (d) Nolan, S. P.; Lopez de la Vega, R.; Mukerjee, S. L.; Hoff, C. D. *Inorg. Chem.* **1986**, *25*, 1160–1165. (e) Mukerjee, S. L.; Nolan, S. P.; Lopez de la Vega, R.; Hoff, C. D. *Inorg. Chem.* **1988**, *27*, 81–85.