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Reactions of Titanium- and Zirconium(III) Complexes with Unsaturated Organic Systems. X-ray Structure of $\{[(\eta^5\text{-}C_5H_5)Zr(CH_3)]_2[\mu\text{-}\eta^1\text{-}\eta^2\text{-}CN(Me_2C_6H_3)](\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)\}$

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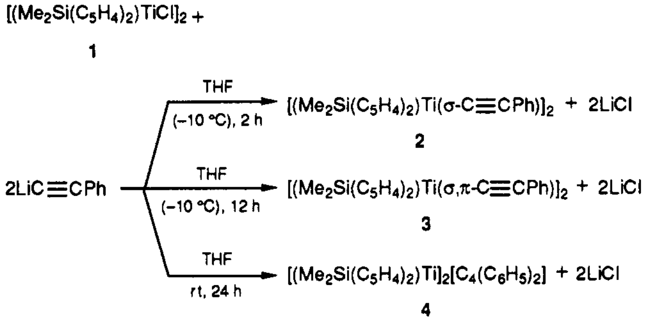
The reaction of $\{[Me_2Si(C_5H_4)_2]TiCl\}_2$ with LiC≡CPh takes place with C—C coupling of the acetylide ligand to give a dimeric titanium(IV) complex containing a bridging 1,4-diphenyl-1,3-butadiene group. Two intermediates were isolated from this reaction, one containing σ-C≡CPh units and the other consisting of two bridging –C≡CPh groups σ and π bound to both metal centers. In a similar reaction of $\{[(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)\}$ with LiC≡CPh only the compound with σ,π-C≡CPh groups was isolated. This complex shows a high Zr═C alkylidene character with what are essentially Zr(IV) centers. The same zirconium(III) derivative also reacts with 2,6-dimethylphenyl isocyanide, leading to the oxidative addition of the isocyanide ligand to give an imine dimeric complex containing bridging η^1-η^2 groups with C and N coordinated to both zirconium atoms, $\{[(\eta^5\text{-}C_5H_5)ZrCl]_2[\mu\text{-}\eta^1\eta^2\text{-}CN(2,6\text{-}Me_2C_6H_3)](\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)\}$. The alkylation of this compound with MeLi produces the dimethyl derivative which was studied by X-ray diffraction methods, and its crystal structure is reported. The compound crystallizes in the monoclinic space group $P2_1/n$, with $Z = 8$, $a = 14.739$ (4) Å, $b = 20.583$ (7) Å, $c = 17.535$ (5) Å, and $\beta = 103.77$ (1)°. Anisotropic refinement of all atoms, except hydrogen, converged to the residuals $R = 0.053$, $R_w = 0.058$ for 6448 observed reflections. The two zirconium atoms are bonded together by fulvalene and isocyanide groups.

Introduction

The chemical and structural behavior of dialkyl metallocenes Cp_2MR_2 (M = Ti, Zr, Hf; R = alkynyl) has been extensively studied,[1-3] but similar mononuclear metal(III) species are unknown with the exception of $Cp^*_2Ti(C{\equiv}CMe)$, recently reported by Teuben.[4a] Reactions of titanium(III) halides with acetylides[4b,5] or those of dialkyl metallocenes (Zr, Hf) with the corresponding metallocene "Cp_2M" fragments generated in situ[2,6] have been reported. Neither of these two methods lead to mononuclear metal(III) species, and depending ôn the metal, different reaction pathways were observed. The alkynyltitanium(III) complexes, initially formed, dimerize with C–C coupling of the acetylide ligand via intermediate species, occasionally isolated,[3,5] containing bridging groups. Use of zirconium and hafnium leads to metallocyclic systems with a significant shortening of the metal–carbon distances.[2]

We report here the reaction with LiC≡CPh of $[(Me_2SiCp_2)TiCl]_2$, for which the particular characteristics of the ansa silylbis(cyclopentadienyl) ligand allows the isolation and characterization of two intermediates. The corresponding zirconium complex is not known[12] and not many similar zirconium complexes can be used for comparison. We report the reaction of LiC≡CPh with the easily accessible dinuclear fulvalene complex $\{[(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)\}$,[9,10] along with its reaction with 2,6-di-*tert*-butylphenyl isocyanide and the alkylation with MeLi of the resulting product.

Scheme I



Results and Discussion

Reactions of $[(Me_2Si(C_5H_4)_2)TiCl]_2$ with LiC≡CPh. This reaction leads to different products depending on the solvent, temperature, time of reaction, and presence of light.

When the reaction was carried out in a molar Ti/Li ratio of 1/1 in THF at −40 °C, a red-garnet solution was immediately formed. After stirring for 2 h in the dark between −40 and −10 °C, complex **2** was obtained. When solutions of **2** were stirred for 12 h under the same conditions, compound **3** was formed. However, when the reaction was allowed to warm to room temperature, the initial color changed to dark green and complex **4** resulted. All three complexes have the same analytical composition but show a quite different structural behavior. The formation of these compounds is deeply dependent on the solvent. Thus, solutions of isolated red **3** in acetone were immediately transformed into the green **4**.

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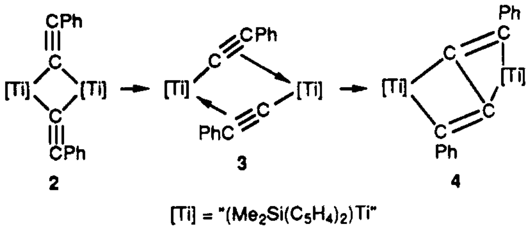
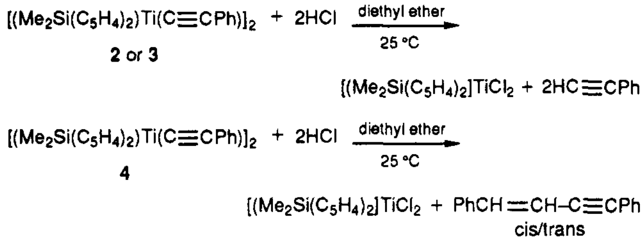
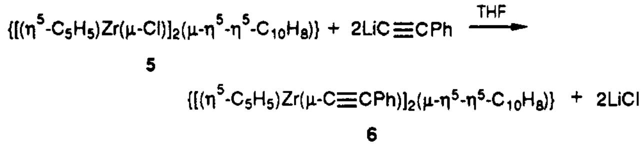
Scheme II



Scheme III



Scheme IV



Complexes 2 and 3 are soluble in THF and slightly soluble in aromatic solvents and hydrocarbons. They decompose rapidly in chlorinated solvents and are very air sensitive. Compound 4 is slightly soluble in ethers and aromatic solvents and insoluble in hydrocarbons. It is stable and soluble in chloroform and dichloromethane and remains unaltered in dry oxygen although it reacts slowly in the presence of moisture. Whereas 2 is a paramagnetic compound, 3 and 4 are diamagnetic.

Structural information was deduced from IR spectroscopy. The three compounds show characteristic absorptions of the $Me_2Si(C_5H_4)_2$ ring system (see Experimental Section), but they show significant differences in absorptions due to the stretching ν(C≡C) vibrations. Complex 2 shows a medium-intensity absorption at 2068 cm^{-1}, as expected[4] for a σ-alkynyl group. This absorption appears at 1769 cm^{-1} for complex 3, which shows a behavior similar to that known for $[Cp_2TiC{\equiv}CSiMe_3]_2$,[3] and is consistent with a bridging alkynyl group σ and π coordinated to two titanium atoms. The coordination of the acetylene system to a second metal atom decreases the C—C bond order, thus shifting the absorption to lower frequencies.[2] No ν(C≡C) absorption was observed in the IR spectrum of 4.

The mass spectrum for complex 4 confirms its dimeric nature, the molecular ion being observed at m/e 670 along with the monomeric fragment which appears at m/e 335.

The ^{1}H NMR spectrum of 3 in benzene-d_6 shows four multiplets at δ 5.70, 5.58, 5.43, and 5.34 for the unequivalent C_5H_4 ring protons, along with two singlets at δ 0.37 and 0.20 due to the magnetically different methylsilyl protons. A similar spectral behavior is also observed for 4, with all of the resonances shifted to lower field, as expected for a complex containing the metal atom in a higher oxidation state. This behavior is consistent with an ABCD spin system for the ring protons with loss of the C_{2v} symmetry of the Cp_2M unit. A ^{1}H NMR spectrum could not be recorded for the paramagnetic complex 2.

The pathway in Scheme II can be proposed for the reaction.

The addition of acetylide initially leads to the formation of the kinetic complex 2, which according to its paramagnetic behavior could be formulated as a mononuclear species or a dinuclear compound containing a bridging σ Ti–C bond. A noticeable feature of these particular ligands, when bonded to electron-deficient metal atoms, is the tendency to coordinate the unsaturated system. This explains the easy conversion of 2 into the thermodynamically stable 3 at low temperatures. The diamagnetic character of 3 is probably due to an antiferromagnetic coupling through both bridging acetylene bonds rather than to a metal–metal interaction, as observed for similar titanium(III) complexes.[3,7] The intramolecular rearrangement of 3 to give an oxidative C–C coupling leads to the formation of 4 and seems to be very favorable, taking place rapidly at room temperature. According to the proposed mechanism for this type of oxidative coupling,[5] the presence of the bridging ansa (dimethylsilyl)bis(cyclopentadienyl) group stabilizes the oxidation state (III).[12] This effect favors the stabilization of the two intermediates which can be isolated and characterized in a unique reaction sequence.

The different nature of the three complexes was confirmed by their reaction with HCl(g).

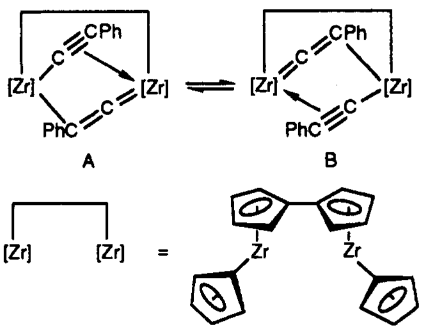
Diethyl ether solutions of 2 and 3 react with bubbling HCl, producing the dichloro ansa metallocene quantitatively with liberation of phenylacetylene. Complex 4 also reacts with HCl giving the metallocene, but the liberated organic product is a mixture, ca. 3/7, of cis/trans isomers of 1,4-diphenylbutenyne as identified by ^{1}H NMR spectroscopy.[8]

Reaction of {[$(C_5H_5)Zr(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)$} (5) with LiC≡CPh. The reaction of this zirconium(III) fulvalene complex with LiC≡CPh in a 1/2 molar ratio in THF at room temperature gives orange 6.

Complex 6 is insoluble in aliphatic hydrocarbons, slightly soluble in benzene and toluene, and soluble in THF and dichloromethane. It does not react with oxygen and remains unmodified in air for days.

The mass spectrum of 6 shows the parent molecular ion at m/e 640 (100%). Its IR spectrum shows the ν(C≡C) stretching vibration at 1807 cm^{-1}, indicating that the acetylene bond of the alkenyl ligand is π-coordinated to a second zirconium atom, thus acting as a σ–π bridging ligand. The ^{1}H NMR spectrum in benzene-d_6 shows one singlet at δ 5.55 for the cyclopentadienyl ring protons along with two other resonances that have an intensity ratio of 1/1; these can be assigned to the fulvalene protons. One of them appears as a triplet at δ 4.73 (J = 2.6 Hz), whereas the second is a nonresolved broad multiplet at δ 5.05. The ^{13}C NMR spectrum in THF-d_8 shows three resonances at δ 106.7, 102.9, and 98.1. The low-field signal is assignable to the fulvalene C_1 atom, and the resonance due to the cyclopentadienyl carbon atoms is coincident at δ 102.9 with that due to one pair of fulvalene carbon atoms. The acetylene phenyl group gives resonances in the range δ 130–135. The most noticeable signals are those due to the acetylene C_α and C_β atoms which appear in the proton-coupled ^{13}C NMR spectrum as one singlet at δ 211.2 and one triplet at δ 144.0 (J_{C-H} = 4.57 Hz), respectively. This behavior is similar to that known[2,6] for dinuclear complexes of the type $(Cp_2Zr)_2(C{\equiv}CR)_2$, but different from that described for dialkynyl metallocenes $Cp_2Zr(C{\equiv}CR)_2$. So, our complex 6 must adopt a dinuclear structure with one bridging fulvalene group, one cyclopentadienyl ring bound to each zirconium atom, and two acetylene bridging ligands π-coordinated to one metal center and σ-coordinated to the other one with a high alkylidene character, as shown

Scheme V



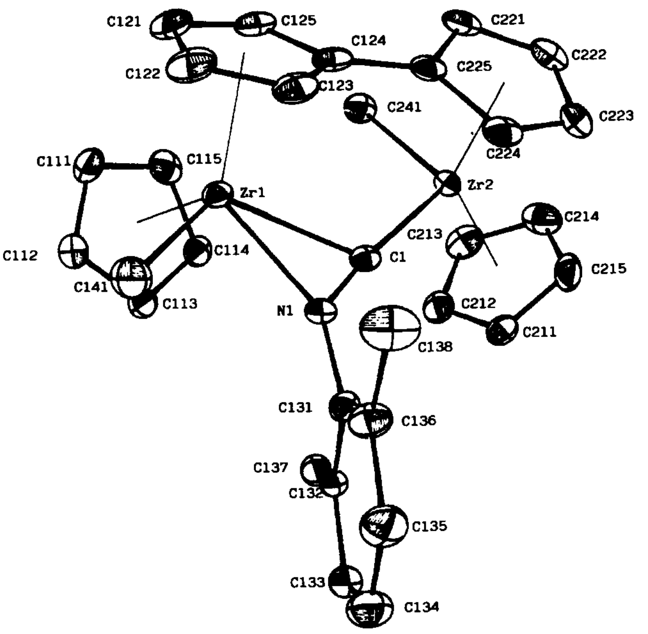


Figure 1. Molecular view of 8 with the atom-numbering scheme.

by the two resonance structures drawn in Scheme V.

Reaction of $\{[(C_5H_5)Zr(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)\}$ (5) with 2,6-$Me_2C_6H_3NC$. This reaction is analogous to that previously reported[11] between the same zirconium(III) complex and 2,6-di-*tert*-butylphenyl isocyanide and leads to the oxidative addition of the isocyanide ligand to give 7. Complex 7 was alkylated with MeLi in toluene giving 8 whose molecular structure was studied by X-ray diffraction methods.

Complexes 7 and 8 were characterized by IR, ^1H, and ^{13}C NMR spectroscopy. Their structural behavior is similar to that reported for the 2,6-di-*tert*-butylphenyl isocyanide derivative, as shown in the Experimental Section. The most noticeable features are the presence of nonequivalent cyclopentadienyl rings and C_5H_4 fulvalene fragments, along with the lack of equivalence of all the protons and carbon atoms from each fragment. The resonance due to the cyanide carbon atom appears at δ 219.1 for 7; however it is not observed for 8. The Zr–methyl protons of 8 are observed as two singlets at δ +0.23 and –0.18.

Structure of $\{[(\eta^5\text{-}C_5H_5)Zr(CH_3)]_2[\mu\text{-}\eta^1\text{-}\eta^2\text{-}CN(Me_2C_6H_3)](\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)\}$ (8). The molecular structure of 8 is reported. An ORTEP view is shown in Figure 1 along with the atomic labeling system. In the asymmetric unit of the unit cell there are two crystallographically independent molecules, both being essentially identical. Only the labeling of molecule 1 is shown. Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are presented in Table I for both molecules 1 and 2. The most representative bond distances and angles are given in Table II.

Table I. Positional Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*, Å^2
Zr(1)	0.79624 (4)	0.28176 (3)	0.10617 (4)	3.36 (1)
Zr(2)	0.53095 (4)	0.29562 (3)	0.01985 (4)	3.07 (1)
N(1)	0.7149 (3)	0.3509 (2)	0.1632 (3)	2.9 (1)
C(1)	0.6505 (4)	0.3291 (3)	0.1073 (4)	2.9 (1)
Zr(3)	1.14703 (4)	–0.04836 (3)	0.20811 (4)	3.78 (1)
Zr(4)	1.39567 (4)	0.01976 (3)	0.21714 (4)	3.39 (1)
N(2)	1.2691 (3)	–0.0892 (2)	0.2967 (3)	3.1 (1)
C(2)	1.3092 (4)	–0.0473 (3)	0.2648 (4)	3.3 (1)
C(111)	0.8990 (5)	0.2834 (3)	0.0095 (5)	5.5 (2)
C(112)	0.9267 (4)	0.3366 (4)	0.0577 (5)	5.2 (2)
C(113)	0.8539 (4)	0.3804 (3)	0.0447 (4)	4.4 (2)
C(114)	0.7804 (4)	0.3560 (3)	–0.0109 (4)	4.0 (2)
C(115)	0.8078 (5)	0.2952 (3)	–0.0345 (4)	5.0 (2)
C(121)	0.8392 (5)	0.1622 (3)	0.1022 (5)	5.7 (2)
C(122)	0.8431 (6)	0.1761 (3)	0.1809 (5)	6.0 (2)
C(123)	0.7518 (5)	0.1901 (3)	0.1882 (5)	5.1 (2)
C(124)	0.6899 (5)	0.1846 (3)	0.1140 (4)	3.7 (2)
C(125)	0.7459 (5)	0.1687 (3)	0.0613 (4)	4.7 (2)
C(131)	0.7149 (4)	0.3994 (3)	0.2229 (4)	3.4 (1)
C(132)	0.7141 (4)	0.4642 (3)	0.2013 (4)	3.8 (1)
C(133)	0.7246 (4)	0.5109 (3)	0.2616 (5)	4.9 (2)
C(134)	0.7341 (5)	0.4941 (4)	0.3387 (5)	6.2 (2)
C(135)	0.7322 (6)	0.4293 (4)	0.3579 (5)	5.9 (2)
C(136)	0.7221 (5)	0.3809 (3)	0.3002 (4)	4.7 (2)
C(137)	0.6997 (4)	0.4871 (3)	0.1187 (4)	4.2 (2)
C(138)	0.7184 (7)	0.3114 (4)	0.3258 (5)	6.6 (2)
C(211)	0.4721 (4)	0.4081 (3)	0.0323 (4)	4.1 (2)
C(212)	0.5108 (4)	0.4094 (3)	–0.0319 (5)	4.8 (2)
C(213)	0.4566 (5)	0.3722 (4)	–0.0912 (5)	5.6 (2)
C(214)	0.3859 (5)	0.3454 (4)	–0.0621 (5)	6.5 (2)
C(215)	0.3951 (4)	0.3683 (3)	0.0130 (5)	5.6 (2)
C(221)	0.5267 (5)	0.1739 (3)	0.0279 (4)	4.8 (2)
C(222)	0.4378 (5)	0.1972 (3)	0.0305 (5)	5.5 (2)
C(223)	0.4452 (5)	0.2315 (3)	0.1000 (5)	5.3 (2)
C(224)	0.5373 (5)	0.2302 (3)	0.1407 (4)	4.5 (2)
C(225)	0.5897 (4)	0.1943 (3)	0.0958 (4)	3.8 (1)
C(311)	1.0982 (5)	0.0689 (3)	0.2091 (5)	6.5 (2)
C(312)	1.1537 (5)	0.0569 (3)	0.2827 (5)	5.9 (2)
C(313)	1.1068 (5)	0.0124 (3)	0.3197 (5)	5.7 (2)
C(314)	1.0220 (4)	–0.0018 (4)	0.2673 (5)	5.7 (2)
C(315)	1.0151 (5)	0.0333 (4)	0.2007 (5)	6.3 (2)
C(321)	1.0637 (5)	–0.0591 (4)	0.0654 (5)	6.6 (2)
C(322)	1.1455 (5)	–0.0204 (4)	0.0666 (5)	5.7 (2)
C(322)	1.2232 (5)	–0.0643 (3)	0.0919 (4)	4.4 (2)
C(324)	1.1870 (5)	–0.1249 (3)	0.1076 (4)	5.0 (2)
C(325)	1.0890 (6)	–0.1218 (4)	0.0898 (5)	6.2 (2)
C(331)	1.3063 (4)	–0.1327 (3)	0.3610 (4)	3.2 (1)
C(332)	1.3147 (4)	–0.1984 (3)	0.3474 (4)	4.0 (2)
C(333)	1.3410 (4)	–0.2398 (3)	0.4122 (5)	4.9 (2)
C(334)	1.3596 (5)	–0.2166 (4)	0.4865 (5)	5.5 (2)
C(335)	1.3536 (4)	–0.1516 (4)	0.4995 (4)	5.1 (2)
C(336)	1.3263 (4)	–0.1073 (3)	0.4369 (4)	3.8 (2)
C(337)	1.3197 (5)	–0.0372 (4)	0.4551 (4)	5.0 (2)
C(338)	1.2990 (5)	–0.2261 (3)	0.2655 (4)	5.1 (2)
C(411)	1.4914 (5)	0.0188 (4)	0.3559 (5)	5.0 (2)
C(412)	1.4430 (5)	0.0787 (4)	0.3480 (5)	5.5 (2)
C(413)	1.4771 (5)	0.1167 (3)	0.2956 (5)	5.6 (2)
C(414)	1.5444 (5)	0.0812 (4)	0.2679 (5)	5.9 (2)
C(415)	1.5530 (4)	0.0207 (4)	0.3072 (5)	5.3 (2)
C(421)	1.3583 (5)	0.0056 (4)	0.0715 (5)	5.2 (2)
C(422)	1.4551 (5)	0.0035 (4)	0.0964 (5)	5.4 (2)
C(423)	1.4806 (5)	–0.0519 (3)	0.1426 (4)	4.5 (2)
C(424)	1.3982 (5)	–0.0847 (3)	0.1462 (4)	4.3 (2)
C(425)	1.3220 (4)	–0.0490 (3)	0.1013 (4)	4.2 (2)
C(441)	1.3051 (5)	0.1086 (3)	0.1698 (5)	5.7 (2)
C(341)	1.0733 (5)	–0.1376 (4)	0.2506 (5)	5.5 (2)
C(141)	0.9091 (5)	0.3098 (4)	0.2183 (5)	6.2 (2)
C(241)	0.5790 (5)	0.2612 (3)	–0.0903 (4)	4.5 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Scheme VI

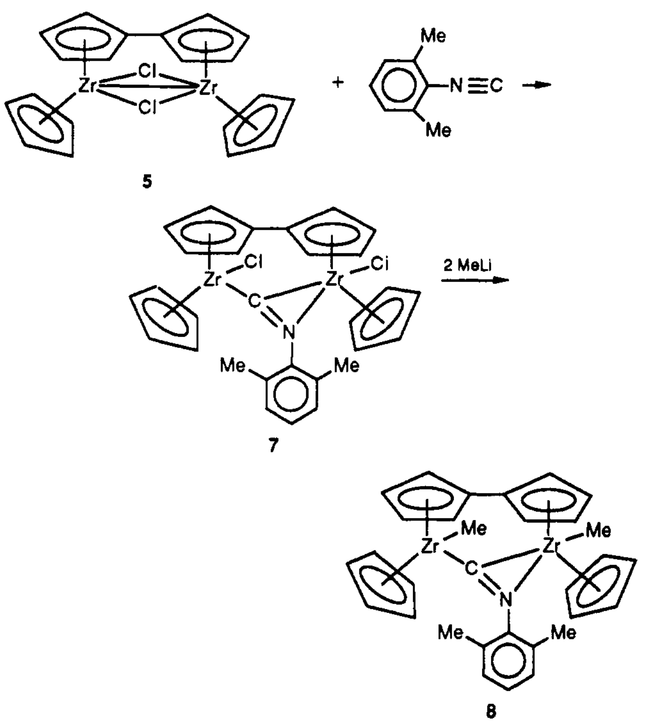


Table II. Selected Bond Distances (Å) and Bond Angles (deg)[a]

molecule 1		molecule 2	
Zr(1)-C(1)	2.363 (6)	Zr(3)-C(2)	2.361 (5)
Zr(1)-N(1)	2.243 (5)	Zr(3)-N(2)	2.242 (4)
Zr(1)-C(141)	2.326 (8)	Zr(3)-C(341)	2.343 (8)
Zr(2)-C(1)	2.155 (5)	Zr(4)-C(2)	2.176 (6)
Zr(2)-C(241)	2.319 (8)	Zr(4)-C(441)	2.298 (6)
Zr(1)-Cp(1)	2.247	Zr(3)-Cp(5)	2.230
Zr(1)-Cp(2)	2.241	Zr(3)-Cp(6)	2.239
Zr(2)-Cp(3)	2.213	Zr(4)-Cp(7)	2.215
Zr(2)-Cp(4)	2.194	Zr(4)-Cp(8)	2.194
C(1)-N(1)	1.273 (7)	C(2)-N(2)	1.250 (8)
N(1)-C(131)	1.450 (8)	N(2)-C(331)	1.442 (7)
Zr(1)-C(1)-Zr(2)	117.0 (3)	Zr(3)-C(2)-Zr(4)	118.1 (2)
C(1)-N(1)-C(131)	131.7 (5)	C(2)-N(2)-C(331)	130.2 (5)
Zr(2)-C(1)-N(1)	173.8 (5)	Zr(4)-C(2)-N(2)	172.7 (4)

[a] Cp(1) is the centroid of C(121)C(122)C(123)C(124)C(125). Cp(2) is the centroid of C(111)C(112)C(113)C(114)C(115). Cp(3) is the centroid of C(221)C(222)C(223)C(224)C(225). Cp(4) is the centroid of C(211)C(212)C(213)C(214)C(215). Cp(5) is the centroid of C(321)C(322)C(323)C(324)C(325). Cp(6) is the centroid of C(311)C(312)C(313)C(314)C(315). Cp(7) is the centroid of C(421)C(422)C(423)C(424)C(425). Cp(8) is the centroid of C(411)C(412)C(413)C(414)C(415).

The structure consists of two zirconium atoms π-bonded to the fulvalene ligand, and each zirconium atom is further bonded to a Cp ring and a methyl group. The ligand phenyl isocyanide is found between the two zirconium atoms. If the ring centroids are considered as coordination sites, Zr(2) is actually a pseudotetrahedral Cp_2ZrL_2-type complex, whereas Zr(1) is a pseudopentacoordinate Cp_2ZrL_3-type species and this different steric crowding defines their structural differences. Thus, in molecule 1 the average Zr(1)–C(η^5) distances (2.532 Å for Cp and 2.544 Å for fulvalene) and also the Zr(1)–centroid distances (2.241 and 2.247 Å, respectively) are slightly longer than those corresponding to Zr(2)–C(η^5) (2.504 and 2.496 Å) and Zr(2)–centroid (2.194 and 2.213 Å). On the other hand, the Zr(2)–C(1) bond distance, 2.155 (5) Å [2.176 (6) Å] (hereafter the values in brackets refer to molecule 2), is substancially shorter than the Zr(1)–C(1) distance, 2.363 (6) Å [2.361 (5) Å], this Zr(2)–C(1) distance being one of the shortest distances reported so far. The Zr–methyl bond length is slightly shorter in Zr(2)–C(241), 2.319 (8) Å [2.298 (6) Å], than in Zr(1)–C(141), 2.326 (8) Å [2.343 (8) Å], and is intermediate between those reported for complexes containing Zr–C(sp^3) bonds [2.279 (4) Å in $(\eta^5\text{-}C_5H_5)_2Zr(CH_2SiMe_3)_2$, 2.294 (8) Å in $(\eta^5\text{-}C_5H_5)_2Zr(CH_2CMe_3)_2$.[13] 2.431 Å in $(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-}Me_2NCHCHPPh_2)(CH_3)$,[14] and 2.357 Å in $(\eta^5\text{-}C_5H_5)_2Zr(\eta^2\text{-}MeNNCPh_2)(CH_3)$[15]].

The Zr(1)–N(1) bond length is 2.243 (5) Å [2.242 (4) Å], and the N(1)–C(1) distance is 1.273 (7) Å [1.250 (8) Å]. All these distances are in agreement with the values reported for the similar chloro compound containing the *tert*-butylimine group.[11] The Zr(1)–N(1) bond distance is intermediate between those found for internal and external Zr–N in η^2-hydrazonide complexes.[15,16] The chain Zr(2)–C(1)–N(1) is fairly linear with an angle of 173.8 (5)° [172.7 (4)°]. The C(1)–N(1)–C(131) angle of the initially isocyanide ligand has been reduced to 131.7 (5)° [130.2 (5)°], as corresponds to an imine group which shows a C=N bond distance of 1.273 (7) Å [1.250 (8) Å].

The difference in the average C–C distances and the thermal parameters in both cyclopentadienyl and fulvalene rings, which has been assigned by Bernal[17] and Lappert[13] to the "thermal motion" of the rings, is too small to be discussed.

The angle between the two C_5H_4 planes of the fulvalene ligand is 19.5 (5)° [16.8 (7)°] and the angles between the C_5H_5 and half-fulvalene C_5H_4 planes bonded to the same zirconium atom are 49.9 (3)° [48.7 (4)°] for Zr(1) and 47.0 (2)° [47.9 (3)°] for Zr(2). The distances from Zr to Cp centroids are 2.241 and 2.247 Å [2.239 and 2.230 Å] for Zr(1) and 2.194 and 2.213 Å [2.194 and 2.215 Å] for Zr(2); these angles and distances are nominally smaller for the Zr not bonded to the N atom. The methyl groups are located trans with respect to the line Zr···Zr, this distance being 3.853 (2) Å [3.892 (2) Å], corresponding to a nonbonding interaction.

Conclusions

The different behaviors of titanium(III) and zirconium(III) are evident from the reactions of their cyclopentadienyl derivatives with LiC≡CPh. Both react to give diamagnetic titanium(IV) and zirconium(IV) complexes, but a C–C coupling reaction of the alkynyl ligand takes place for titanium, whereas an alkylidene derivative is obtained for zirconium. The reaction with the ansa (dimethylsilyl)bis(cyclopentadienyl)titanium derivative permits the isolation of two intermediate products postulated for these type of processes. One contains bridging σ-alkynyl ligands whereas the second contains a bridging σ–π system.

The fulvalene zirconium complex also reacts with isocyanides to give $\mu\text{-}\eta^1\text{-}\eta^2$-coordinated ligands oxidatively added to the two zirconium atoms of a dinuclear species. It can be methylated without modification of the bridging

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ligand, as shown by its X-ray crystal structure.

Experimental Section

All manipulations were performed under an inert atmosphere (dinitrogen or argon) using Schlenk and high-vacuum line techniques or a glovebox Model HE-63-P (Pedetrol). Solvents were purified by distillation from an appropriate drying/deoxygenated agent (sodium/benzophenone for THF and diethyl ether, sodium for toluene, sodium/potassium alloy for hexane, and $CaCl_2$ for acetone). $(Me_2Si(C_5H_4)_2)TiCl_2$,[18] $[(Me_2Si((C_5H_4)_2)TiCl]_2$,[12] $LiC{\equiv}CPh$,[19] and $\{[(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)\}$[9] were prepared according to literature procedures. MeLi was purchased from Fluka. NMR spectra were recorded on Varian FT-80A and Varian Unity FT-300 instruments. ^1H and ^{13}C chemical shifts were referenced to Me_4Si. Mass spectra were recorded on a Hewlet-Packard 5890 spectrometer. IR spectra were performed (Nujol mulls) on a 883 Perkin-Elmer spectrophotometer (in the IR spectra the presence of the C_5H_4[20] unit from (dimethylsilyl)cyclopentadiene and fulvalene and Me_2Si[21] in (dimethylsilyl)cyclopentadiene were identified according to literature references). Elemental C, H analyses were carried out on a Perkin-Elmer 240B microanalyzer.

Synthesis of $[(Me_2Si(C_5H_4)_2)Ti(\sigma\text{-}C{\equiv}CPh)]_2$ (2). To a cooled (−40 °C) mixture of $(Me_2Si(C_5H_4)_2)TiCl_2$ (0.50 g, 1.64 mmol) and 0.042 g (1.80 mmol) of Na/Hg (10%) in THF (50 mL) was added a solution of $LiC{\equiv}CPh$ (0.177 g, 1.64 mmol) in THF (15 mL). The reaction mixture was stirred at −10 °C for 2 h. The solvent was eliminated under vacuum to give a residue which was washed with 50 mL of cold toluene. After filtration the resulting solution was concentrated to 15 mL. Cooling to −30 °C gave **2** as red crystals (0.15 g, 27.6% yield).

IR (Nujol/CsI): $\nu(C{\equiv}C) = 2068\ cm^{-1}$. Anal. Calcd for $C_{20}H_{19}SiTi$ (found): C, 71.64 (71.33); H, 5.67 (5.23).

Synthesis of $\{[Me_2Si(C_5H_4)_2]Ti(\sigma,\pi\text{-}C{\equiv}CPh)\}_2$ (3). To a cooled (−20 °C) mixture of $(Me_2Si(C_5H_4)_2)TiCl_2$ (0.50 g, 1.64 mmol) and 0.042 g (1.8 mmol) of Na/Hg (10%) in THF (50 mL) was added a solution of $LiC{\equiv}CPh$ (0.177 g, 1.64 mmol) in THF (20 mL). The reaction mixture was warmed to room temperature and stirred at −10 °C over a period of 12 h. The solvent was eliminated under vacuum to give a residue which was washed with 50 mL of cold toluene. The resulting solution was filtered and concentrated to 15 mL. After cooling to −30 °C, compound **3** was obtained as a black red microcrystalline solid (0.23 g, 42.3% yield).

IR (Nujol/CsI): $\nu(C{\equiv}C) = 1769\ cm^{-1}$. Anal. Calcd for $C_{20}H_{19}SiTi$ (found): C, 71.64 (71.42); H, 5.67 (5.43). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 0.20 (s, 3 H, CH_3–Si), 0.37 (s, 3 H, CH_3–Si), 5.34 (m, 2 H, C_5H_4), 5.43 (m, 2 H, C_5H_4), 5.58 (m, 2 H, C_5H_4), 5.70 (m, 2 H, C_5H_4), 7.26–7.13 (m, 5 H, C_6H_5).

Synthesis of $\{[(Me_2Si(C_5H_4)_2)Ti]_2[C_4(C_6H_5)_2]\}$ (4). Method A. To a cooled (−40 °C) mixture of $(Me_2Si(C_5H_4)_2)TiCl_2$ (0.50 g, 1.64 mmol) and 0.042 g (1.8 mmol) of Na/Hg (10%) in THF (50 mL) was added a solution of $LiC{\equiv}CPh$ (0.177 g, 1.64 mmol) in THF (20 mL). The reaction mixture was warmed to room temperature and then stirred over a period of 24 h. The color turned from red to light green. After filtration the solution was evaporated to dryness and the residue obtained was washed with hot toluene (50 mL). The resulting solution was concentrated to a small volume. Green crystals of **4** precipitated after cooling at −30 °C (0.31 g, 57% yield).

Method B. A 0.30-g (0.45 mmol) amount of $[(Me_2Si(C_5H_4)_2)Ti(\sigma,\pi\text{-}C{\equiv}CPh)]_2$ (**3**) was dissolved in dry acetone (30 mL). The color of the solution immediately changed from red to light green, and the resulting solution was concentrated to a small volume. Cooling at −30 °C gave **4** as a green microcrystalline solid (0.29 g, 97% yield).

IR (Nujol/CsI): $\nu(C{\equiv}C)$ not observed. Anal. Calcd for $C_{20}H_{19}SiTi$ (found): C, 71.64 (71.17); H, 5.67 (5.79). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 0.70 (s, 3 H, CH_3–Si), 0.71 (s, 3 H, CH_3–Si), 5.10 (m, 2 H, C_5H_4), 5.24 (m, 2 H, C_5H_4), 6.17 (m, 2 H, C_5H_4), 6.26 (m, 2 H, C_5H_4), 7.51 (m, 5 H, Ph). EI-MS (70 eV): m/z = 670 [M^+] (17.8%); m/z = 234 [$(Me_2SiCp_2)Ti^+$] (100%).

Reaction of $[(Me_2Si(C_5H_4)_2)Ti(C{\equiv}CPh)]_2$ (2 or 3) with $HCl_{(g)}$. HCl(g) was bubbled through a solution of $[(Me_2Si(C_5H_4)_2)Ti(C{\equiv}CPh)]_2$ (**2** or **3**) (0.30 g, 0.45 mmol) in diethyl ether (30 mL) with vigorous stirring. The color turned light red within 2–3 min. The resulting solution was evaporated to yield a red solid which was identified as $(Me_2Si(C_5H_4)_2)TiCl_2$ (0.26 g, 96% yield from **2** and 0.24 g, 91% yield from **3**). The solvent evaporated was trapped at liquid nitrogen temperature, and the fractional distillation permitted the separation of phenylacetylene ($PhC{\equiv}CH$, bp 142 °C).

Reaction of $\{[(Me_2Si(C_5H_4)_2)Ti]_2[C_4(C_6H_5)_2]\}$ (4) with $HCl_{(g)}$. HCl(g) was bubbled through a solution of 0.3 g (0.45 mmol) of $\{[(Me_2Si(C_5H_4)_2)Ti][C_4(C_6H_5)_2)]\}$ (**4**) in diethyl ether (30 mL) with vigorous stirring. The color turned from green to light red within 2–3 min. The resulting solution was filtrated and chromatographed through a silica gel-60 column (0.063–0.200 mm) using hexane as eluent. The solvent was eliminated under vacuum to give a white solid containing a mixture of *cis*- and *trans*-1,4-diphenylbutenyne (ratio 30.3/69.7; 0.91 g, 91% yield).

Synthesis of $\{[(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}C{\equiv}CPh)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)\}$ (6). To a 150-mL flask containing $\{[(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)\}$ (0.66 g, 1.28 mmol) in 50 mL of THF at −78 °C was added dropwise a solution of $LiC{\equiv}CPh$ (0.29 g, 2.7 mmol) in THF (15 mL). The reaction mixture was allowed to warm to room temperature and stirred for 2 days. The resulting solution was evaporated to dryness under vacuum, and the residue obtained was extracted with 100 mL of toluene. After filtration an orange-yellow solution resulted. The solution volume was reduced to 20 mL. Cooling at −30 °C produced compound **6** as an orange microcrystalline solid (0.66 g, 80% yield).

IR (Nujol/CsI): $\nu(C{\equiv}C) = 1807\ cm^{-1}$. Anal. Calcd for $C_{36}H_{28}Zr_2$ (found): C, 67.24 (67.12); H, 4.39 (4.56). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 4.73 (t, 4 H, C_5H_4), 5.05 (br, 4 H, C_5H_4), 5.55 (s, 10 H, C_5H_5), 7.28 (m, Ph), 7.60 (m, Ph). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 98.10 [$C_{2,5}$ ($C_{10}H_8$)], 102.90 [$C_{3,4}$ ($C_{10}H_8$) + C_5H_5], 106.7 [C_1 ($C_{10}H_8$)], 127.14, 129.5, 131.61 [C_2, C_3, C_4 (Ph)], 135.5 [C_1 (Ph)], 144.0 [C_β ($C{\equiv}C$)], 211.21 [C_α ($C{\equiv}C$)]. EI-MS (70 eV): m/z = 640 (100%).

Synthesis of $\{[(\eta^5\text{-}C_5H_5)ZrCl]_2[\mu\text{-}\eta^1\text{-}\eta^2\text{-}CN(2,6\text{-}Me_2C_6H_3)](\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)\}$ (7). A solution of 2,6-dimethylphenyl isocyanide (0.13 g, 0.99 mmol) in toluene (15 mL) was added to a solution of $\{[(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}Cl)]_2(\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)\}$ in 40 mL of toluene at room temperature. The color immediately changed from dark red to violet. The resulting solution was stirred over a period of 4 h. After filtration, the solution was concentrated to a small volume by evaporation of the solvent. Upon cooling to −30 °C, violet crystals of **7** were obtained (0.57 g, 89% yield).

IR (Nujol/CsI): $\nu(CN)$ = 1605 and 1580 cm^{-1}. Anal. Calcd for $C_{29}H_{27}NZr_2Cl_2$ (found): C, 54.18 (53.87); H, 4.24 (4.03); N, 2.18 (2.04). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 2.16 (s, 3 H, CH_3–Ph), 2.46 (s, 3 H, CH_3–Ph), 5.56 (s, 5 H, C_5H_5), 5.96 (s, 5 H, C_5H_5), 4.45, 4.88, 5.24, 5.49, 5.63, 5.69, 6.41 and 6.54 (8 m, 8 × 1 H, $C_{10}H_8$), 6.88 (m, Ph). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 18.96 and 21.0 (CH_3), 109.29 and 110.97 (C_5H_5), 101.22, 102.21, 103.33, 103.77, 107.23, 111.71, 113.96 and 115.66 ($C_{10}H_8$), 219.11 (CN).

Synthesis of $\{[(\eta^5\text{-}C_5H_5)Zr(CH_3)]_2[(\mu\text{-}\eta^1\text{-}\eta^2\text{-}CN(Me_2C_6H_3)](\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)\}$ (8). A solution of MeLi in diethyl ether (0.62 mL, 1.6 M) was added by syringe to a cooled (− 78 °C) solution containing 0.32 g (0.5 mmol) of $\{[(\eta^5\text{-}C_5H_5)ZrCl]_2[\mu\text{-}\eta^5\text{-}\eta^5\text{-}CN(Me_2C_6H_3)](\mu\text{-}\eta^5\text{-}\eta^5\text{-}C_{10}H_8)\}$ (**7**) in 30 mL of toluene. The reaction mixture was slowly warmed to room temperature and then stirred for 12 h. A red solution was obtained, which after filtration was evaporated to dryness under vacuum. The residue was extracted with 20 mL of hexane. The resulting solution was cooled to −30 °C for 12 h. Crystals of **8** suitable for X-ray diffraction were obtained (0.19 g, 63.3% yield).

IR (Nujol/CsI): $\nu(CN)$ = 1614 and 1583 cm^{-1}. Anal. Calcd for $C_{31}H_{33}Zr_2N$ (found): C, 61.84 (61.59); H, 5.52 (5.41); N, 2.33 (2.10). ^1H NMR (300 MHz, C_6D_6, 25 °C): δ −0.18 (s, 3 H, CH_3–Zr), 0.23 (s, 3 H, CH_3–Zr), 2.08 (s, 6 H, CH_3–Ph), 5.44 (s, 5 H, C_5H_5), 5.49 (s, 5 H, C_5H_5), 4.51, 4.77, 4.87, 5.19, 5.20, 5.48, 6.03 and 6.12 (8 m, 8 × 1 H, $C_{10}H_8$), 6.87 (m, Ph). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 9.59 and 16.28 (CH_3–Zr), 18.9 and 19.82 (CH_3–Ph), 106.46

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Table III. Crystal Data, Experimental Data, and Structure Refinement Procedures for 8

formula	$C_{31}H_{33}N_1Zr_2$
cryst habit	prismatic
cryst size, mm	0.25 × 0.20 × 0.30
symmetry	monoclinic, $P2_1/n$
unit cell determn	least-squares fit from 25 rflns $\theta < 30°$
unit cell dimens	
a, b, c, Å	14.739 (4), 20.583 (7), 17.535 (5)
β, deg	103.77 (1)
packing	
V, Å^3; Z	5166 (5); 8
D_{calc}, g cm^{-3}	1.55
M_r	602.05
$F(000)$	2448
μ, cm^{-1}	8.13
technique	four-circle diffractometer; Enraf-Nonius CAD-4, bisecting geometry, graphite-oriented monochromator, Mo Kα, ω/θ scans; θ_{max} = 27.0°
no. of rflns measd	10681
no. of ind rflns obs	6448, $2\sigma(I)$ criterium
range of hkl	−18 to +18; 0 to 26; 0 to 22
std rflns	2 reflections every 100 reflections no variation
R	0.053
R_w	0.058
goodness of fit indicator	1.72
max peak in final diff map, e/Å^3	0.52
min peak in final diff map, e/Å^3	−1.2

and 106.28 (C_5H_5), 93.94, 98.21, 99.16, 101.37, 101.86, 103.36, 110.99 and 116.33 ($C_{10}H_8$), CN (not observed).

Structure of {[(η^5-C_5H_5)Zr(CH_3)]$_2$[μ-η^1-η^2-CN-($Me_2C_6H_3$)](μ-η^5-η^5-$C_{10}H_8$)} (8). Single crystals of 8 suitable for X-ray studies were obtained by crystallization at −30 °C from a solution of toluene/hexane. A single crystal of 8 was sealed in a Lindemann glass capillary under dry nitrogen and used for data collection. Crystallographic information is listed in Table III. The intensity data were collected at room temperature (22 °C) on an Enraf-Nonius CAD 4 diffractometer. Intensities were corrected for Lorentz and polarization effects. No absorption or extinction corrections were made. The structure was solved by a combination of direct methods and Fourier synthesis and refined (on F) by full-matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically. In the later stages of refinement hydrogen atoms were included at idealized positions from geometric calculations; staggered configurations were assumed for the methyl groups, when necessary, with fixed positions and thermal parameters equivalent to those of the atoms to which they are attached.

Final values of r = 0.053 and R_w = 0.058 with $R_w = [\sum w||F_o| - |F_c||^2|\sum w|F_o|^2]^{1/2}$ and $w = 4F_o^2/[\sigma(F_o)^2]^2$ were obtained. Anomalous dispersion corrections and atomic scattering factors were taken from ref 22. Calculations were performed with the SDP Enraf-Nonius package,[23] MULTAN,[24] and DIRDIF[25] on a Microvax II computer.

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Registry No. **1**, 133672-12-5; **2**, 138207-60-0; **3**, 138180-49-1; **4**, 138207-61-1; **5**, 100946-29-0; **6**, 138180-50-4; **7**, 138180-51-5; **8**, 138180-52-6; LiC≡CPh, 4440-01-1; (*Z*)-PhCH=CHC≡CPh, 13343-78-7; (*E*)-PhCH=CHC≡CPh, 13343-79-8; PhC≡CH, 536-74-3; 2,6-dimethylphenyl isocyanide, 2769-71-3.

Supplementary Material Available: Tables of displacement parameters, positional parameters, and bond distances and angles (31 pages); a listing of structure factors (33 pages). Ordering information is given on any current masthead page.

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