4372 *Organometallics* **2003,** *22,* 4372−4374

(Cyclopentadienylamine)scandium(2,3-dimethyl-1,3-butadiene): A 1,3-Diene Complex of Scandium with Sc(I)- and Sc(III)-like Reactivity

Dirk J. Beetstra, Auke Meetsma, Bart Hessen,* and Jan H. Teuben

Dutch Polymer Institute/Center for Catalytic Olefin Polymerization,
Stratingh Institute for Chemistry and Chemical Engineering, University of Groningen,
Nijenborgh 4, 9747 AG Groningen, The Netherlands

Received April 14, 2003

Summary: The scandium 2,3-dimethyl-1,3-butadiene complex [η^5,η^1-$C_5H_4(CH_2)_2NMe_2$]$Sc(C_6H_{10})$ (**2**) *reacts with PhCN via initial nitrile insertion into the Sc−diene bond to give a dimeric* μ^2*-imido species, but with a 2,2′-bipyridine via the elimination of the free diene. The latter shows that* **2** *can be used to generate the reactive fragment* [η^5,η^1-$C_5H_4(CH_2)_2NMe_2$]Sc^I.

Transition-metal complexes of the 1,3-butadiene ligand and its various substituted derivatives display very interesting features with respect to structure and bonding as well as reactivity. In its complexes, the *s-cis*-1,3-butadiene ligand has been observed to adopt a range of intergraded bonding modes between the η^4-diene (**A**) and σ^2,π-metallacyclopentene (**B**) extremes.[1] These two structures are related by an oxidative addition operation in which the diene in structure **B** is effectively doubly reduced to a but-2-ene-1,4-diyl dianion. The relative importance of the diene or metallacyclopentene character depends on several factors, especially the reducing power of the low-valent metal fragment. Reactivity corresponding to this σ^2,π-metallacyclopentene character includes the insertion of unsaturated substrates into the metal−methylene bond[2] and the attack of Lewis acids such as $B(C_6F_5)_3$ on the diene methylene carbon to yield zwitterionic metal allyl species (which can act as single-component olefin polymerization catalysts).[3] Reactivity associated with η^4-diene character includes the displacement of the neutral diene ligand by various reagents, which can then undergo oxidative addition or oxidative coupling reactions on the resultant low-valent transition-metal species.[2c,d] Many transition-metal diene complexes with intermediate bonding modes show both types of reactivity behavior, depending on the type of reagent used. In contrast, only very few 1,3-diene complexes of the group 3 and lanthanide metals are known. These are practically limited to 1,4-diphenyl-1,3-butadiene derivatives, in which the ligand predominantly has dianionic character and of which little reactivity has been reported.[4] In addition, several naphthalene−lanthanide complexes show structural features consistent with 1,3-diene character.[5]

The group 3 metal scandium has a strong preference for the trivalent oxidation state, although some compounds with the metal in the monovalent oxidation state are known, e.g., in solid ScCl.[6] Recently a Sc^IBr unit sandwiched between two (β-diketiminato)MgBr fragments was reported by Roesky et al.[7] We are exploring the chemistry of Sc diene complexes to see whether “low-valent” behavior for Sc may be induced by the presence of a diene ligand. Here we describe the synthesis and characterization of the first 1,3-butadiene complex of scandium, [η^5,η^1-$C_5H_4(CH_2)_2NMe_2$]Sc(2,3-dimethyl-1,3-butadiene), with some aspects of its reactivity. It is shown that this compound can behave as a source of the reactive [η^5,η^1-$C_5H_4(CH_2)_2NMe_2$]Sc^I fragment.

The colorless cyclopentadienylamine scandium dichloride $\{[C_5H_4(CH_2)_2NMe_2]ScCl_2\}_x$ (**1**) was obtained in 80% yield from the reaction of the corresponding lithium cyclopentadienide with $ScCl_3(THF)_3$, followed by vacuum sublimation.[8] Reaction of the dichloride **1** with (2,3-dimethyl-1,3-butadiene)Mg·$(THF)_2$ in ether, followed by workup at or below 0 °C, afforded the complex [$C_5H_4(CH_2)_2NMe_2$]$Sc(C_6H_{10})$ (**2**) as red crystals in 48% yield by crystallization from pentane.[9]

---

* To whom correspondence should be addressed. E-mail: hessen@chem.rug.nl.

(1) See for a recent discussion of the bonding of 1,3-diene ligands to early transition metals: (a) Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1997**, *16*, 3055. (b) Del Rio, D.; Galindo, A. *J. Organomet. Chem.* **2002**, *655*, 16, and references therein.

(2) For examples involving mono(cyclopentadienyl) group 4 metal 1,3-diene complexes, see: (a) Hessen, B.; Blenkers, J.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1989**, *8*, 2809. (b) Ausema, J. B.; Hessen, B.; Teuben, J. H. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 465. (c) Hessen, B.; Blenkers, J.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1989**, *8*, 830. (d) Hessen, B.; Teuben, J. H. *J. Organomet. Chem.* **1988**, *358*, 135.

(3) (a) Temme, B.; Erker, G.; Karl, J.; Luftmann, R.; Fröhlich, R.; Kotila, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1755. (b) Temme, B.; Karl, J.; Erker, G. *Chem. Eur. J.* **1996**, *2*, 919. (c) Jiménez Pintado, G.; Thornton-Pett, M.; Bouwkamp, M.; Meetsma, A.; Hessen, B.; Bochmann, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2358. (d) Devore, D. D.; Timmers, F. J.; Hasha, D. L.; Rosen, R. K.; Marks, T. J.; Deck, P. A.; Stern, C. L. *Organometallics* **1995**, *14*, 3132.

(4) (a) Mashima, K.; Sugiyama, H.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1581. (b) Kretschmer, W.; Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1093. (c) Kretschmer, W.; Thiele, K.-H. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1304. (d) Emelyanova, N. S.; Trifonov, A. A.; Zakharov, L. N.; Shestakov, A. F.; Struchkov, Y. T.; Bochkarev, M. N. *J. Organomet. Chem.* **1997**, *540*, 1.

(5) For a recent review, see: Bochkarev, M. N. *Chem. Rev.* **2002**, *102*, 2089.

(6) Poeppelmeier, K. R.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 294−297.

(7) Neculai, A. M.; Neculai, D.; Roesky, H. W.; Magull, J.; Baldus, M.; Andronesi, O.; Jansen, M. *Organometallics* **2002**, *21*, 2590.

(8) Synthesis of **1**: A solution of 1.74 g (12.2 mmol) of [$C_5H_4(CH_2)_2NMe_2$]Li and 4.20 g (11.4 mmol) of $ScCl_3(THF)_3$ in 50 mL of THF was stirred overnight. Removal of the volatiles followed by sublimation (42 mTorr, 150 °C) of the residual solid afforded 2.31 g (9.14 mmol, 80%) of **1** as a white crystalline solid. Anal. Calcd $C_{13}H_{22}NCl_2Sc$: C 50.67, H 7.19, N 4.54, Sc 14.59. Found: C 50.27, H 7.05, N 4.37, Sc 14.40. The analogous complex [$C_5Me_4(CH_2)_2NMe_2$]$ScCl_2$ was reported previously: Christopher, J. N.; Squire, K. R.; Canich, J. A. M.; Schaffer, T. D. World Pat. WO 00/18808.

10.1021/om030267h CCC: $25.00

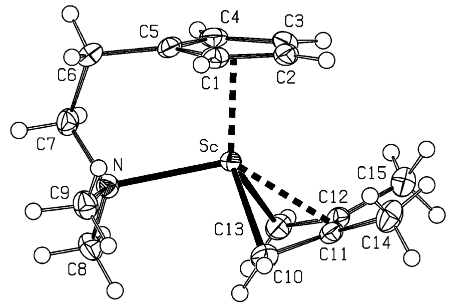


Figure 1. Molecular structure of **2**. Selected interatomic distances (Å) and angles (deg): Sc−N = 2.358(2), Sc−C(10) = 2.249(3), Sc−C(11) = 2.401(2), Sc−C(12) = 2.400(2), Sc−C(13) = 2.251(2), C(10)−C(11) = 1.455(3), C(11)−C(12) = 1.386(3), C(12)−C(13) = 1.464(3), Sc−C(10)−C(11) = 77.6(2), Sc−C(13)−C(12) = 77.3(1).

A crystal structure determination of **2** (Figure 1)[10] showed that the prone-oriented butadiene fragment has considerable 2-ene-1,4-diyl character, as indicated by the relatively short central C−C bond of 1.386(3) Å and relatively long C−CH$_2$ bonds of 1.455(3) and 1.464(3) Å. In the ^{1}H and ^{13}C NMR spectra of **2**, the resonances for the diene methylene groups are observed at δ 1.76 and 2.58 ppm (d, $^2J_{HH}$ = 6.8 Hz) and δ 59.0 ppm ($\Delta\nu_{1/2}$ = 183 Hz, broadened by the quadrupolar ^{45}Sc nucleus, $I = 7/2$), respectively.

In its structural features, the diene complex **2** thus predominantly displays Sc(III) σ^2,π-metallacyclopentene character. In line with this, **2** reacts readily with polar unsaturated substrates to give products that derive from insertion into the Sc−methylene bonds. With 1 equiv of benzonitrile, **2** reacts to give the colorless μ^2-imido complex $\{[C_5H_4(CH_2)_2NMe_2]Sc[\mu^2\text{-}NC(Ph)C_6H_{10}]\}_2$ (**3**), which was characterized by single-crystal X-ray diffraction of crystals of its benzene solvate (Figure 2).[11] The Cp-amine ligands adopt a trans geometry around the central Sc$_2$N$_2$ core, which is practically equilateral. Although common for many transition metals, M$_2$(μ^2-NR)$_2$ species of group 3 metals to our knowledge have not yet been reported and have only very recently been observed for lanthanide metals.[12]

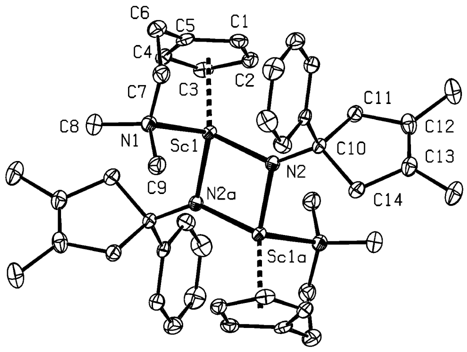
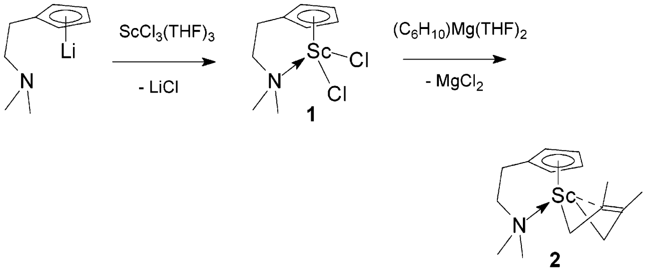
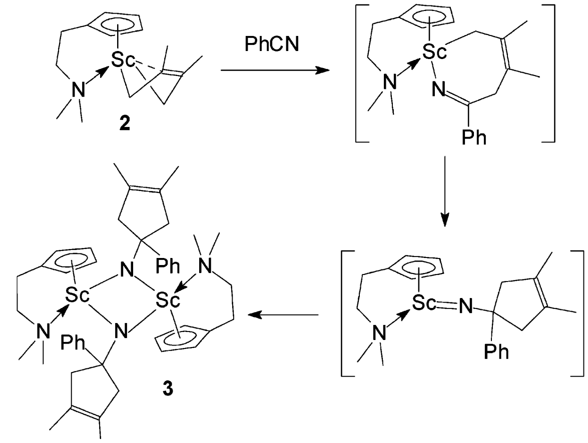


Figure 2. Molecular structure of **3**. Selected interatomic distances (Å) and angles (deg): Sc(1)−N(1) = 2.375(3), Sc(1)−N(2) = 2.017(2), Sc(1)−N(2a) = 2.056(2), N(2)−C(10) = 1.465(3), N(2)−Sc(1)−N(2a) = 87.14(9), Sc(1)−N(2)−Sc(1a) = 92.86(9), Sc(1)−N(2)−C(10) = 138.2(2), Sc(1a)−N(2)−C(10) = 127.6(3).

Scheme 1



Scheme 2



The formation of this product can be explained by the sequence depicted in Scheme 2, in which the nitrile initially inserts into one of the Sc−CH$_2$ bonds, followed by an attack of the other diene methylene group on the carbon atom of the imide intermediate. This yields an electronically unsaturated metal imido species that will readily dimerize. A similar reaction sequence was earlier observed in our group in the reaction of (C$_5$Me$_5$)Hf(2,3-dimethyl-1,3-butadiene)Cl with acetylene, in which case a μ-alkylidene complex was formed.[13]

In contrast with the insertion chemistry described above for the reaction of **2** with benzonitrile, the reaction of **2** with 2 equiv of 4,4′-dimethyl-2,2′-bipyridine leads to liberation of free 2,3-dimethyl-1,3-butadiene (as seen by NMR spectroscopy). From a reaction in toluene, followed by crystallization from hexane, the resulting bis(4,4′-dimethyl-2,2′-bipyridine) adduct $[C_5H_4(CH_2)_2NMe_2]Sc(\eta^2\text{-}N_2C_{12}H_{12})_2$ (**4**) was isolated as a black

---

(9) Synthesis of **2**: A suspension of **1** (220 mg, 0.87 mmol) and (C$_6$H$_{10}$)Mg(THF)$_2$ (295 mg, 1.17 mmol) in 30 mL ether was stirred at 0 °C for 1.5 h. At 0 °C the volatiles were removed in vacuo, and the residue was extracted with pentane. Concentrating the solution and cooling to −80 °C afforded **2** (110 mg, 0.42 mmol, 42%) as red crystals. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 6.20 (ps.t, J = 2.8 Hz, 2H, C$_5$H$_4$), 6.01 (ps.t, J = 2.8 Hz, 2H, C$_5$H$_4$); 2.58 (d, J = 6.8 Hz, 2H, *syn*-CH$_2$); 2.11 (t, J = 6.2 Hz, 2H, CH$_2$), 1.87 (t, J = 6.2 Hz, 2H, CH$_2$), 1.82 (s, 6H, Me), 1.76 (d, J = 6.8, 2H, *anti*-CH$_2$), 1.71 (s, 6H, Me). Anal. Calcd for C$_{15}$H$_{24}$NSc: C 68.66, H 9.22, N 5.34, Sc 16.79. Found: C 68.00, H 9.27, N 5.23, Sc 16.68.

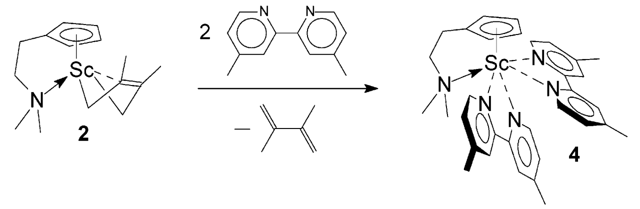
(10) Crystal data for **2**: C$_{15}$H$_{24}$NSc, space group $C2/c$, monoclinic, a = 17.707(1) Å, b = 8.4651(6) Å, c = 19.903(1) Å, β = 105.984(1)°, V = 2868.0(3) Å^3; T = 125(1) K, Z = 8, μ(Mo Kα) = 4.93 cm^{-1}, 13 775 reflections measured (3544 unique), final refinement converged at $R_w(F^2)$ = 0.0975 with 250 parameters.

(11) Crystal data for **3**·(C$_6$H$_6$): (C$_{22}$H$_{29}$N$_2$Sc)$_2$·C$_6$H$_6$, space group $P\bar{1}$, triclinic, a = 8.7222(8) Å, b = 10.5565(9) Å, c = 12.580(1) Å, α = 70.455(2)°, β = 88.427(2)°, γ = 88.719(2)°, V = 1091.05(16) Å^3; T = 110(2) K, Z = 2, μ(Mo Kα) = 3.50 cm^{-1}, 5899 reflections measured (4441 unique), final refinement converged at $R_w(F^2)$ = 0.1232 with 381 parameters.

(12) (a) Chan, H.-S.; Li, H.-W.; Xie, Z. *Chem. Commun.* **2002**, 652. (b) Gordon, J. C.; Giesbrecht, G. R.; Clark, D. L.; Hay, P. J.; Keogh, D. W.; Poli, R.; Scott, B. L.; Watkin, J. G. *Organometallics* **2002**, *21*, 4726.

(13) Hessen, B.; Van Bolhuis, F.; Teuben, J. H. *Organometallics* **1987**, *6*, 1352.

Scheme 3



crystalline material (Scheme 3), which nevertheless was persistently contaminated with free bipyridine.

A crystal structure determination[14] of the compound revealed that the metal center is pseudo-six-coordinate, with one η^5-cyclopentadienyl group, two η^2-bipyridine ligands, and the coordinated pendant amine (Figure 3). The Sc−N(amine) distance of 2.564(4) Å is 0.2 Å longer than that in **2** or **3** in response to the high coordination number of the metal center in **4**. Inspection of the C−C and C−N distances within the 4,4′-dimethyl-2,2′-bipyridine ligands reveals that both ligands appear to be reduced to their radical monoanions (e.g., as seen from the central bipyridine C−C bonds in **4** of 1.41−1.42 Å as compared to 1.48 Å in neutral bipyridine[15]). This indicates that the effective oxidation state of the Sc metal center in **4** is Sc(III), a tribute to the strong reducing power of lower oxidation states of Sc.[16] ^{1}H NMR spectra of solutions of **4** in C_6D_6 show only resonances of some free 4,4′-dimethyl-2,2′-bipyridine (which always seems to be present in samples of **4**), suggesting that the compound is paramagnetic. An Evans method[17] determination of the magnetic moment of **4** on a benzene solution of **4** generated in situ from **2** and 2 equiv of 4,4′-dimethyl-2,2′-bipyridine yielded μ_{eff} = 1.54 (expected spin-only for an $S = 1$ system: μ_{eff} = 2.83). This indicates either a degree of magnetic coupling between the bipyridyl radical anion ligands in **4** or partial decomposition of **4** (e.g., by partial loss of free ligand, a possible source of the persistent presence of 4,4′-dimethyl-2,2′-bipyridine in solid samples). Attempts to drive such a reaction by removal of 4,4′-dimethyl-2,2′-bipyridine from **4** by, for example, vacuum sublimation did not yield well-defined organometallic products.

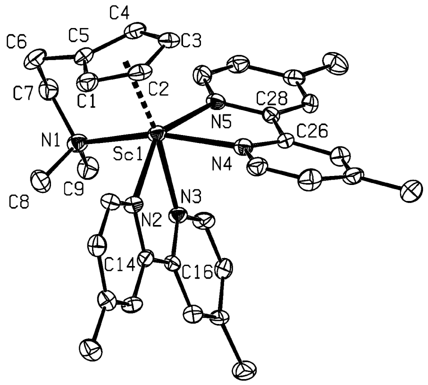


Figure 3. Molecular structure of **4**. Selected interatomic distances (Å) and angles (deg): Sc(1)−N(1) = 2.564(4), Sc(1)−N(2) = 2.272(3), Sc(1)−N(3) = 2.252(3), Sc(1)−N(4) = 2.219(3), Sc(1)−N(5) = 2.228(3), N(2)−C(14) = 1.385(5), N(3)−C(16) = 1.374(5), C(14)−C(16) = 1.410(5), N(4)−C(26) = 1.364(5), N(5)−C(28) = 1.368(5), C(26)−C(28) = 1.422(5), N(1)−Sc(1)−N(4) = 154.3(1), N(2)−Sc(1)−N(5) = 147.5(1), N(2)−Sc−N(4) = 85.6(1).

The scandium diene complex **2** is thus found to be able to eliminate the neutral diene ligand and can act in this way as a precursor for the $[C_5H_4(CH_2)_2NMe_2]Sc^I$ fragment. Preliminary experiments in which **2** was reacted with reagents that are known to give facile oxidative addition to low-valent transition-metal centers (I_2, PhSSPh) showed that also in these cases the diene ligand is readily eliminated, yielding species that, by ^{1}H NMR spectroscopy, appear to be C_s symmetric $[C_5H_4(CH_2)_2NMe_2]ScX_2$ compounds (X = I, SPh). Presently we are investigating the scope of this approach with other group 3 and lanthanide metals.

Supporting Information Available: Experimental details of the preparation and characterization of compounds **1**−**4**, NMR data of preliminary reactivity studies on **2** and X-ray structural data for compounds **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030267H

---

[14] Crystal data for **4**: $C_{33}H_{38}N_5Sc$, space group $P2_1/a$, monoclinic, $a = 9.277(2)$ Å, $b = 17.315(3)$ Å, $c = 17.786(3)$ Å, $\beta = 100.951(3)°$, $V = 2805.0(9)$ Å^3; $T = 100(1)$ K, $Z = 4$, μ(Mo Kα) = 2.94 cm^{-1}, 16 598 reflections measured (3885 unique), final refinement converged at $R_w(F^2) = 0.1316$ with 504 parameters.

[15] See for example: Echegoyen, L.; DeCain, A.; Fischer, J.; Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 838.

[16] Several lanthanide complexes with multiple bipyridyl radical anion ligands have been reported; see for example: Fedushkin, I. L.; Petrovskaya, T. V.; Girgsdies, F.; Nevodchikov, V. I.; Weimann, R.; Schumann, H.; Bochkarev, M. N. *Russ. Chem. Bull.* **2000**, *49*, 1869.

[17] (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Schubert, E. M. *J. Chem. Educ.* **1992**, *69*, 62.