Some Reactions of Transition Metal Amides and Alkoxides with Coordinated Dienes; X-ray Crystal Structure of $(\eta^5\text{-}C_5H_5)_2Zr(NHPh)(OSO_2CF_3)$

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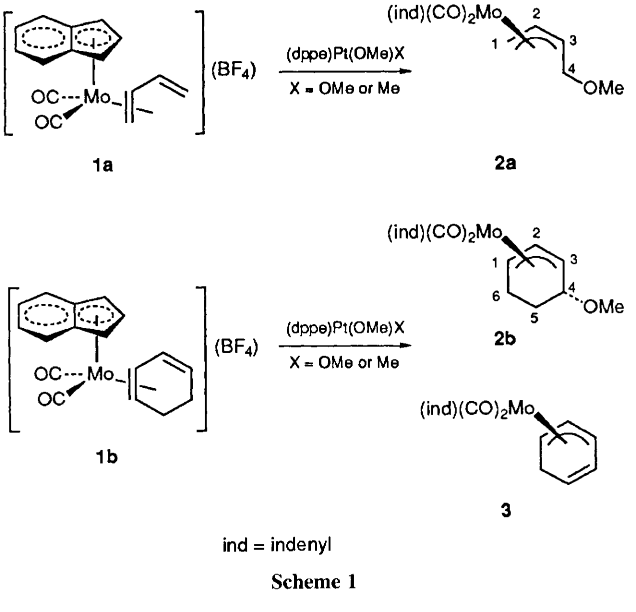
Cationic molybdenum diene complexes undergo nucleophilic attack by both early transition metal amides and late transition metal alkoxides to give π-allyl complexes.

Although the literature concerning nucleophilic attack on coordinated alkenes is vast,[1] there are no examples in which the nucleophile is a transition metal alkoxide or amide; we report the first examples of this reaction type.

Reaction of molybdenum butadiene complex **1a**[2] with $(dppe)Pt(OMe)_2$ [dppe = 1,2-bis(diphenylphosphino)ethane][3] in tetrahydrofuran (THF) gives π-allyl complex **2a**.† Although a complex mixture of Pt containing products is formed, analytically pure **2a** can be isolated from the reaction mixture in 64% yield after recrystallization from



Scheme 1

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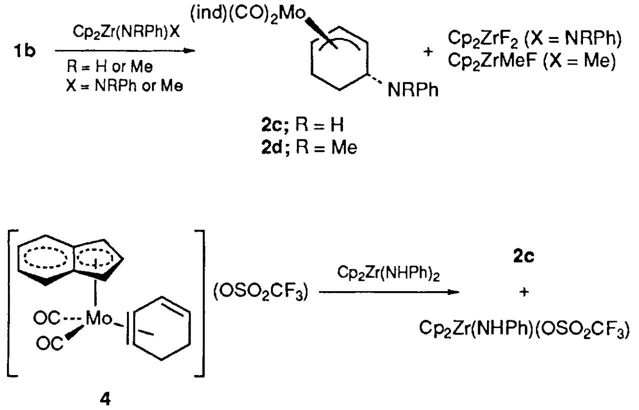
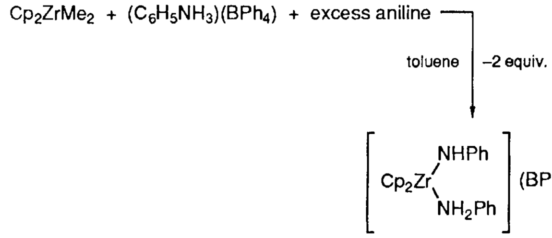
† ^1H NMR assignments for compounds **2a–2c** are based on 2D NMR experiments and comparison with literature data for related compounds (refs. 2 and 5). *Selected spectral data:* **2a** IR (CH_2Cl_2) ν_{CO}/cm^{-1} 1948, 1865; ^1H NMR ($[^2H_8]$THF) δ 7.11 (m, 4H), 6.07 (m, 2H), 5.68 (m, 1H), 3.46 (dd, 1H, *J* 3.5, 11.1 Hz, 4-H), 3.01 (m, 4H, OMe and 3-H), 2.31 (dd, 1H, *J* 1.5, 7.9 Hz, 1-H_{syn}), 1.53 (dd, 1H, *J* 11.1, 11.1 Hz, 4-H′), 1.35 (dd, 1H, *J* 1.5, 11.8 Hz, 1-H_{anti}), −0.10 (dt, 1H, *J* 7.9, 11.7 Hz, 2-H). **2b** IR (CH_2Cl_2) ν_{CO}/cm^{-1} 1940, 1859; ^1H NMR ($[^2H_8]$THF) δ 7.08 (s, 4H), 6.06 (d, 1H, *J* 2.8 Hz), 6.03 (d, 1H, *J* 2.8 Hz), 5.69 (t, 1H, *J* 2.8 Hz), 3.20 (br, 2H, 4-H and 1-H or 3-H), 3.16 (s, 3H, OMe), 3.01 (br, 1H, 1-H or 3-H), 1.85 (m, 1H, 6-H_{exo}), 1.42 (ddd, 1H, *J* 3.1, 6.7, 14.5 Hz, 6-H_{endo}), 1.00 (dd, 1H, *J* 5.9, 14.6 Hz, 5-H_{exo}), 0.39 (m, 1H, 5-H_{endo}), −0.40 (t, 1H, *J* 7.2 Hz, 2-H). **2c** IR (CH_2Cl_2) ν_{NH}/cm^{-1} 3418, ν_{CO}/cm^{-1} 1940, 1860; ^1H NMR ($[^2H_8]$THF) δ 7.05 (s, 4H), 6.95 (t, 2H, *J* 8.5 Hz, H_{meta}), 6.43 (m, 3H, H_{ortho} and H_{para}), 6.10 (d, 1H, *J* 2.8 Hz), 6.06 (d, 1H, *J* 2.8 Hz), 5.71 (t, 1H, *J* 2.8 Hz), 4.56 (br d, 1H, *J* 8.3 Hz, NH), 3.45 (br m, 1H, 4-H), 3.18 (br d, 1H, *J* 6.7 Hz, 1-H or 3-H), 3.12 (br d, 1H, *J* 7.2 Hz, 1-H or 3-H), 1.87 (m, 1H, 6-H_{exo}), 1.45 (m, 1H, 6-H_{endo}), 0.96 (dd, 1H, *J* 5.7, 14.0 Hz, 5-H_{exo}), 0.46 (m, 1H, 5-H_{endo}), −0.54 (t, 1H, *J* 7.3 Hz, 2-H).



Scheme 2



(1)

THF–pentane. Similarly, reaction of (dppe)Pt(OMe)Me[3] with **1a** gives **2a**. Reaction of (dppe)Pt(OMe)$_2$ with cyclohexa-1,3-diene complex **1b**[2] gives **2b**, contaminated by approximately 10% of π-allyl complex **3**[4] (derived from deprotonation of the cyclohexadiene ligand). The reaction of (dppe)Pt(OMe)Me with **1b** gives **2b** and **3** in an approximately 1 : 1 ratio (Scheme 1). ^{1}H NMR data for **2b** are consistent with methoxide adding to the *exo* face of the diene.[5a] The rates of these reactions (complete within minutes at 25 °C) suggest that they proceed *via* nucleophilic attack by the Pt–O bond on the coordinated diene, rather than by nucleophilic attack by free methoxide.‡

We had expected that the electron-rich platinum methoxide complexes would display nucleophilic reactivity towards coordinated alkenes.[6] More surprising was the observation that zirconocene amides do so as well. For example, reaction of Cp$_2$Zr(NHPh)$_2$§ with molybdenum cyclohexadiene complex **1b** proceeds rapidly at 25 °C to give π-allyl complex **2c** and Cp$_2$ZrF$_2$ in quantitative yield (Scheme 2), as judged by ^{1}H NMR spectroscopy. Pure **2c** can be isolated from the reaction mixture in 53% yield after recrystallization from THF–pentane. Similarly, reaction of Cp$_2$Zr(NHPh)Me[7] with **1b** gives **2c** and Cp$_2$ZrMeF.[8] Reaction between Cp$_2$Zr(NMePh)$_2$§ and **1b** gives **2d** and Cp$_2$ZrF$_2$. Again, the reaction is quantitative by ^{1}H NMR spectroscopy. However, in concentrated solution **2d** decomposes to give, among other products, *N*-methylaniline and **3**; we have been unable to isolate it in pure form. ^{1}H NMR data for **2c** and **2d** are consistent with the amide adding to the *exo* face of the diene.[5a]

A plausible mechanism for these reactions involves nucleophilic attack by the polar Zr–N bond on the coordinated diene's terminal carbon to give the Mo π-allyl complex and a cationic zirconocene amido or methyl complex. The latter could then abstract fluoride from its BF$_4^-$ counterion to give Cp$_2$Zr(NRPh)F or Cp$_2$ZrMeF and BF$_3$. Reaction between Cp$_2$Zr(NRPh)F and BF$_3$ gives Cp$_2$ZrF$_2$ and F$_2$BNRPh.[9] Cationic zirconocene amido complexes are reasonable intermediates: we have prepared the cationic zirconocene amido [Cp$_2$Zr(NHPh)(NH$_2$Ph)](BPh$_4$) by the reaction shown in eqn. (1), and found that it reacts rapidly with (NEt$_4$)(BF$_4$) to give Cp$_2$ZrF$_2$.

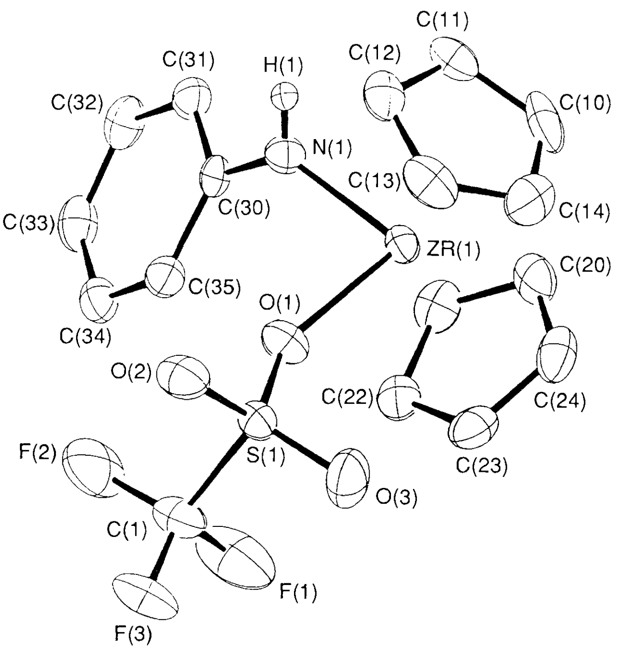


Fig. 1 Structure of Cp$_2$Zr(NHPh)(OSO$_2$CF$_3$). Selected distances (Å) and angles (°): Zr(1)–O(1) 2.162 (3), Zr(1)–N(1) 2.072 (3), N(1)–C(30) 1.415 (5), N(1)–H(1) 0.744 (33), O(1)–Zr(1)–N(1) 92.3 (1), Zr(1)–O(1)–S(1) 150.2 (2), Zr(1)–N(1)–C(30) 133.4 (3), Zr(1)–N(1)–H(1) 114 (3), C(30)–N(1)–H(1) 112 (3).

Formation of strong Zr–F bonds is not a necessary driving force for the reactions discussed above, since Cp$_2$Zr(NHPh)$_2$ reacts with trifluoromethanesulphonate salt **4** to give **2c** and Cp$_2$Zr(NHPh)(OSO$_2$CF$_3$). The X-ray crystal structure of the zirconium product is shown in Fig. 1.¶ It is the first zirconium complex with a primary amido ligand to be characterized crystallographically. The Zr–O distance is long (2.162 Å). The dihedral angle between the planes defined by Zr–O–S and N–Zr–O is 14.7°, which, in addition to the long Zr–O distance, implies that there is little π-interaction between zirconium and oxygen.[10] The Zr–N distance is normal (2.072 Å), and the anilido ligand is oriented in a manner that enhances π-donation to zirconium [dihedral angle between Zr–N–C(30) and N–Zr–O = 74.3°].

The above reactions are the first examples of nucleophilic attack by transition metal alkoxides and amides on coordinated alkenes. These results are interesting in the light of the fact that, in general, transition metal alkoxides and amides do not react readily with alkenes,[11] and suggest that alkene amination and hydration catalysed by bimetallic transition metal systems may be possible.

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‡ Bryndza and coworkers have estimated the maximum rate of methoxide dissociation from (dppe)Pt(OMe)X (X = Me, OMe) to be 10^{-6} s^{-1} at 25 °C (ref. 3). The reactions reported here are qualitatively much faster.

§ Prepared by reaction of Cp$_2$ZrCl$_2$ with 2 equiv. LiNRPh in THF.

¶ Compound **4** can also be prepared by addition of 1 equiv. of trifluoromethanesulphonic acid to Cp$_2$Zr(NHPh)$_2$ in THF. *Crystal data* for **4**: ZrC$_{17}$H$_{16}$SF$_3$O$_3$N, monoclinic, $P2_1/n$ (No. 14), a = 9.510(2), b = 12.672(1), c = 14.956(3) Å, β = 102.45(1)°, from 25 reflections, T = −70 °C, V = 1760.0 Å^3, Z = 4, M_r = 462.60, D_c = 1.746 g cm^{-3}. A yellow, irregular plate, ~0.25 × 0.09 × 0.25 mm, obtained from THF–pentane solution, was used for data collection. 4372 reflections were collected in the range 2.8° ≤ 2θ ≤ 55.0° with scan width = 1.20–1.90 ° ω and scan speed = 1.50–5.00° min^{-1}. Final R = 0.035, R_w = 0.035, error of fit = 1.25, max Δ/σ = 0.02. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

We thank Tim Onley and Will Marshall for skilled technical assistance, and Drs Henry E. Bryndza and Rocco A. Paciello for helpful discussions.

Received, 14th September 1990; Com. 0/04214E

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