New Zirconium Phosphido Complexes and Their Reactions with Alkenes

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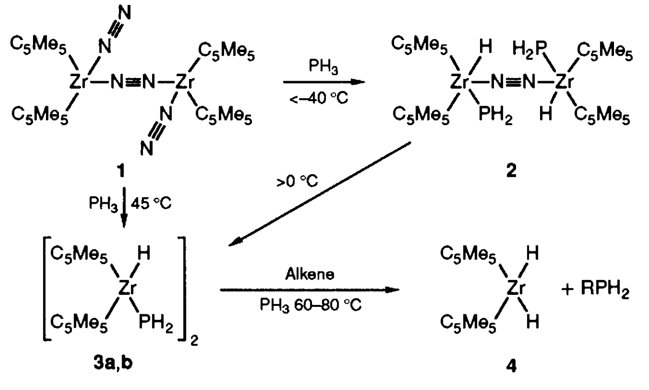
The reaction of PH_3 with the bispentamethylcyclopentadienyl zirconium dinitrogen complex $[\{Zr(C_5Me_5)_2(N_2)\}_2(\mu\text{-}N_2)]$ **1** produces the orange and the yellow phosphido complexes $[\{Zr(C_5Me_5)_2(PH_2)(H)\}_2(\mu\text{-}N_2)]$ **2** and $[\{Zr(C_5Me_5)_2(PH_2)(H)\}_2]$ **3**; the reaction of these complexes with alkenes and PH_3 leads to the selective formation of primary alkyl phosphines, under the mildest conditions of temperature and pressure reported to date.

The catalysis of the addition of P–H bonds to alkenes that would be efficient under mild conditions of pressure and temperature is of interest. Since zirconium complexes are well known to react with and catalyse reactions of alkenes,[1] and zirconium phosphides, although rare, are known to undergo insertions with small molecules (*e.g.* CO),[2] we have investigated reactions of Bercaw's dinitrogen complex[1] **1** with PH_3 in the presence and absence of alkenes.

The reaction of PH_3 with **1** proceeds at low temperature (−40 °C) to give deep orange solutions from which orange crystals may be isolated. Elemental analyses are consistent with the stoichiometry $[\{Zr(C_5Me_5)_2(PH_2)(H)\}_2(N_2)]_2$. If samples of this orange complex are stored (room temperature, 2–3 days), a yellow colour develops and yellow needles may be readily isolated. These conform by elemental analysis to $[\{Zr(C_5Me_5)_2(PH_2)(H)\}_2]$ **3**.

The ^{31}P NMR spectrum[†] of **2** indicates the presence of a $-PH_2$ unit (triplet, δ −92, $J_{P\text{-}H}$ 182.3 Hz; $^{31}P\{^1H\}$ NMR is a singlet). The ^{15}N NMR spectrum (of ^{15}N enriched samples) of **2** shows a single resonance centred at δ −136.4 (δ_A of an AA′XX′ spin system, X = P) with only N–P coupling being evident. Since there is only one resonance we propose that the N_2 ligand is symmetrically bridging in contrast with **1** where the terminal N_2 ligands give rise to two resonances and the chemical shift of the bridging N_2 (δ −118) is similar to that in our compound.[4] The ^1H NMR[‡] spectrum shows the presence of the C_5Me_5 ligands as well as a complex resonance of at least 16 lines centred at δ −7.58 (the outer lines separated by 201.8 Hz) assigned to hydride. This appears as δ_A in an $AA'M_2M'_2XX'$ pattern owing to coupling between the hydride protons and both the phosphorus (X) and phosphido proton (M). The IR spectrum clearly shows a P–H stretch (2301 cm^{-1}) and an M–H stretch (1741 cm^{-1}), as well as the expected ligand absorptions. Thermogravimetric analysis indicates the presence of and subsequent loss of a bridging dinitrogen unit (3% of the total mass).

If solutions of **2** are warmed they become yellow and yellow crystals of **3** may be isolated (Scheme 1). The half life of the conversion of **2** to **3** is *ca.* 45 min at 45 °C in benzene solution (^{31}P NMR). The ^{31}P NMR spectrum of **3** shows a binomial triplet (δ −102, $J_{P\text{-}H}$ 181.2 Hz), indicating the presence of a $-PH_2$ unit (as for **2** the $^{31}P\{1H\}$ NMR spectrum is a singlet). The ^{15}N NMR of **3** prepared from ^{15}N-enriched **2** is featureless. The ^1H NMR spectrum shows the expected C_5Me_5 resonances (δ + 2.00) as well as a complex resonance assigned to the hydride (δ −4.14). Although monomeric analogues {of the form $[Zr(C_5Me_5)_2(X)(PR_2)]^5$} are known, the complexity of the ^1H NMR spectrum of **3** is probably better explained by a dimeric structure and thus the hydride resonance becomes δ_A in an $AA'M_2M'_2XX'$ spin system (M = PH_2, X = P). We propose that **3** is likely best described as having one of two isomeric structures **3a** and **b** (Fig. 1); unfortunately with the



Scheme 1 Reactions of $[\{Zr(C_5Me_5)_2(N_2)\}_2(\mu\text{-}N_2)]$ **1** with PH_3 and alkenes

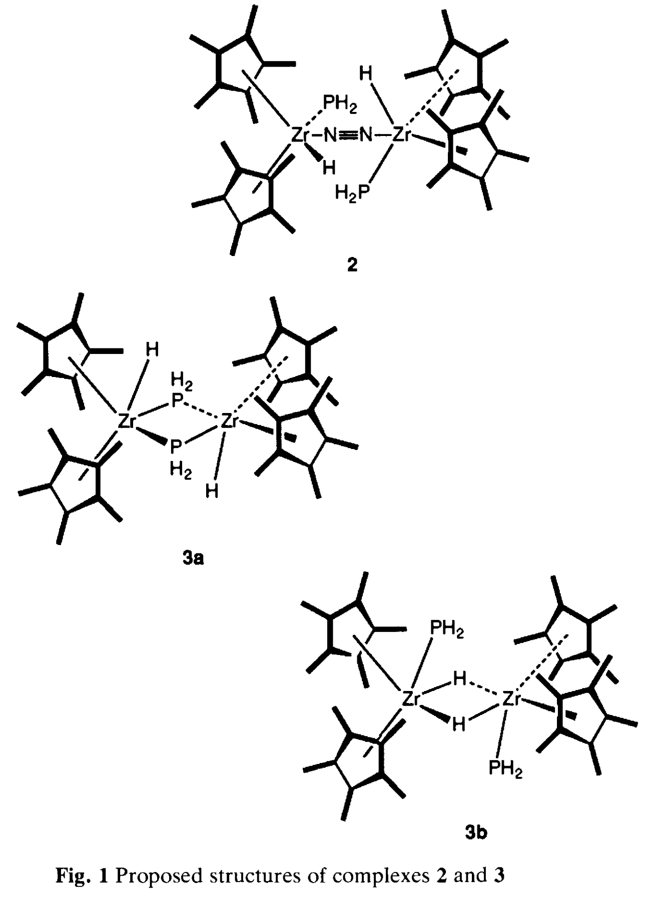


Fig. 1 Proposed structures of complexes **2** and **3**

[†] All ^{31}P and $^{31}P\{^1H\}$ NMR spectra were obtained in C_6D_6, unless otherwise stated, on a JEOL FX90Q instrument operating at 36.23 MHz and were referenced to 85% H_3PO_4 (δ 0). ^1H NMR spectra were obtained on a Bruker WM360 spectrometer and were referenced to residual protons in the solvent, C_6D_6.

[‡] ^1H NMR (δ) **2**: 2.0 (d, 30H, C_5Me_5) and −7.36 (m, 2H, ZrH); **3**: 1.81 (d, 30H, C_5Me_5) and −4.14 (m, 2H, ZrH); for both **2** and **3** discrete resonances assignable to PH_2 were not observed presumably owing to low intensity and complex coupling (and/or) broadening.

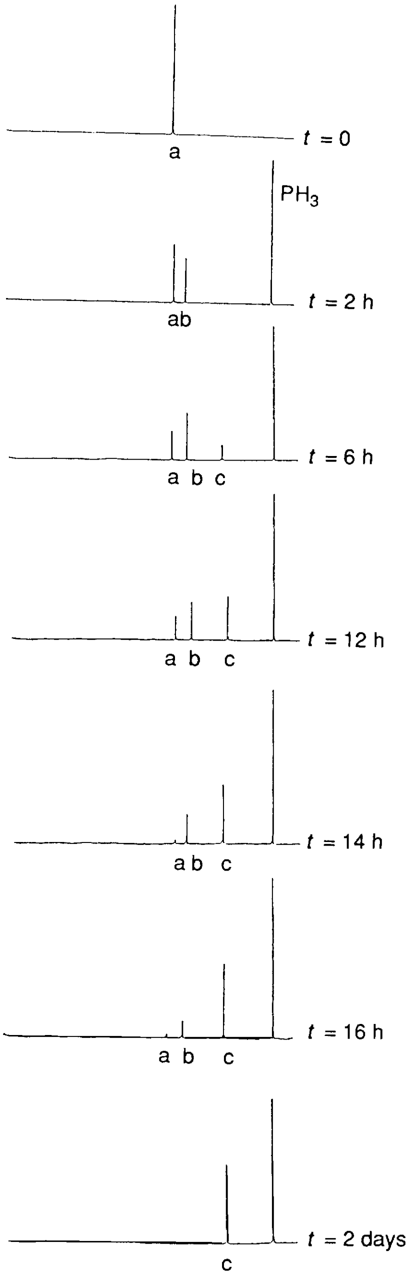


Fig. 2 $^{31}P\{^1H\}$ NMR spectra of the reaction mixture of **2** with an excess of hex-1-ene under PH_3. *Conditions:* $P(PH_3)$ 100 psi; $T = 50$ °C throughout. NMR spectra of all samples were recorded at 27 °C and atmospheric pressure. The spectrum at $t = 0$ is of the reaction mixture before charging with PH_3. The peaks are assigned as follows: (*a*), δ −92, $[\{Zr(C_5Me_5)_2(PH_2)(H)\}_2(N_2)]$; (*b*), δ −102, $[\{Zr(C_5Me_5)_2(PH_2)_2\}_2(H)_2]$; (*c*), δ −141, 1-hexylphosphine; δ −243, PH_3.

lack of suitable comparisons, ^{31}P NMR data do not distinguish between terminal and bridging phosphide.

The IR spectrum shows a P–H stretch (2297.5 cm^{-1}) and M–H stretch (1750 cm^{-1}); thermogravimetric analysis is similar to that for **2** with the exception of the absence of an initial mass loss assignable to loss of N_2.

Thermal decomposition of **3** in solution (120 °C) caused the yellow solution to turn green with the evolution of a white vapour. The $^{31}P\{^1H\}$ NMR spectrum of the residue showed now peaks at δ −10.2 and −16.9 with several weaker signals above δ −200 indicating the presence of P_2H_4 (diphosphine δ −214) and other phosphorus hydrides. The peak at δ − 102 is greatly diminished in intensity and further strong heating leads to its eventual disappearance. The loss of P–H bonds is also confirmed by IR spectroscopy. Thus **3** decomposes completely above 160 °C *via* reductive eliminations.

The reactions of **2** and **3** with several alkenes have been investigated. Initial studies carried out at ambient temperature and pressure under a nitrogen atmosphere confirm that **2** does not react with alkenes. At elevated temperatures the conversion of **2** to **3** occurred, and above 120 °C decay products became evident.§ No evidence was found to indicate that a direct combination of alkene and $(PH_2)^-$ was occurring.

However, under PH_3,¶ and in the presence of hex-1-ene, the outcome of the reaction was different. The formation of 1-hexylphosphine accompanied a drop in pressure, which was found to correspond to an approximately 1 : 1 stoichiometry of Zr complex with PH_3, and loss of solution colour. 1-Hexylphosphine was identified by ^{31}P NMR spectroscopy (δ −141), confirmed by comparison with a sample prepared by reduction of 1-hexyl(diisopropyl)phosphonate with $LiAlH_4$. The presence of **3** was also confirmed. The reaction can be followed by NMR spectroscopy (Fig. 2) and the conversion of **2** to **3** [peaks (*a*) and (*b*), respectively, in spectra 2–7 in Fig. 1] as well as the formation of 1-hexylphosphine with concomitant decay of zirconium phosphides is clearly demonstrated. The selectivity of the reaction is very high, with no trace of secondary or tertiary phosphines or 2-hexylphosphine (by NMR) being formed under these conditions. The reactions with other alkenes give rise to similar results such that under similar conditions, the reaction of **3** with styrene produces phenylmethylphosphine ($^{31}P\{^1H\}$: δ −138) and with cyclohexene gives cyclohexylphosphine ($^{31}P\{^1H\}$: δ −132). It is possible to isolate from the reaction mixture a pale-cream coloured crystalline solid; needles may be isolated from toluene which have identical properties to those of the previously reported hydride $[Zr(C_5Me_5)_2(H)_2]$[6] **4**. Since the formation of alkylphosphine is stoichiometric in zirconium complex, the source of the hydrido protons in **4** is probably the alkene since performing the reaction in deuteriated solvent or with PD_3 does not result in the deuterido analogues of **4**.

We are currently investigating the mechanism of this reaction in more detail, as well as similar studies of other metal systems.

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References

1 For examples see: J. A. Labinger and W. P. Anderson, *J. Organomet. Chem.*, 1977, **138**, 185; E. Negishi and D. E. van Horn, *J. Am. Chem. Soc.*, 1978, **100**, 2252.
2 D. M. Roddick, B. D. Santarsiero and J. E. Bercaw, *J. Am. Chem. Soc.*, 1985, **107**, 4670.
3 J. E. Bercaw, D. R. McAlister and J. M. Manriquez, *J. Am. Chem. Soc.*, 1978, **100**, 3078.
4 J. M. Manriquez, D. R. McAlister, E. Rosenberg, A. M. Shiller, S. I. Chan and J. E. Bercaw, *J. Am. Chem. Soc.*, 1978, **100**, 3078.
5 G. A. Vaughan and G. L. Hillhouse, *Organometallics*, 1989, **8**, 1760.
6 J. E. Bercaw, *Adv. Chem. Ser.*, 1977, **167**, 136.

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§ This reaction was carried out with styrene, cyclohexene and hex-1-ene. The ^{31}P NMR spectra of these reactions showed the following results: styrene: δ −242.7, −18.1 and −14.3; cyclohexene: δ −243.2, −20.8 and −14.07; hex-1-ene: δ 243.2, −18.9 and −12.02.

¶ 80 psi, 100 °C: half life *ca.* 6.5 h, *i.e.* half the maximum yield of 1-hexylphosphine. The reaction occurs under milder conditions but more slowly (*e.g.* Fig. 2; 80 psi, 50 °C: half life *ca.* 10.5). Higher pressures of PH_3 allow higher reaction temperatures (and faster rates) before decomposition is observed.