

Dimerization of Metastable Metallo-methylenephosphanes to Dimetalla-diphosphabicyclobutane and Metallo-diphosphacyclohexenone Derivatives

Hans Jürgen Metternich,^a Edgar Niecke*^a and John F. Nixon^b

^a Anorganisch-Chemisches Institut der Universität Bonn, Gerhard-Domagk-Strasse 1, W-5300 Bonn 1, Germany

^b School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, UK

Reactions of Cl-P=C(SiMe₃)₂ with K[FeCp(CO)₂] and K[FeC₃H₅(CO)₃] afford the first examples of metastable metallo-methylenephosphanes, which dimerize at low temperatures.

The synthesis and reactivity of metallo-methylenephosphanes is still attracting a great deal of interest.¹ The intrinsic stability of these coordination compounds is strongly influenced by the nucleophilic nature of the metal centre and the steric features of the ligands bonded in the organometallic fragment. Thus, increasing electron density at the metal atom (Mo < Fe < Ni) and decreasing size of the ligand (C₃H₅ < C₅H₅ < C₅Me₅) results in a decreasing thermal stability of the corresponding metallo-methylenephosphanes L_nM-P=CR₂.² Here, we report on the first dimerization products of iron complexes containing a P=C moiety acting as a one-electron donor.

In a typical preparation³ a tetrahydrofuran (thf) solution of the chloro-methylenephosphane **1**⁴ was treated at -70 °C with an equimolar amount of K[Fe(η⁵-Cp)(CO)₂] in tetrahydrofuran. After being warmed to room temperature, the red-brown reaction mixture was filtered and evaporated to dryness. Crude **3** remained after the work-up procedure as a dark red, viscous oil. All attempts to isolate **3** have failed so far owing to its thermal instability. However, elucidation of the constitution of the metallo-methylenephosphane **3** was possible on the basis of NMR spectroscopy.[†] The extreme deshielding of the ³¹P NMR signal of **3** (δ 593.2) and the characteristic low-field ¹³C resonance (δ 211.2, *J* 110.9 Hz) indicated the presence of a metal-substituted P=C double bond.¹⁻³ The dimerization of **3** to give **7** is complete within 10 days and seemed to proceed *via* an initial [2+1] cycloaddition step to give **4**. The formation of **7** might involve nucleophilic attack of the P^V=C carbon atom in **4** at one carbonyl group of the transition metal fragment **5** followed by a 1,3-trimethylsilyl shift **6** and incorporation of a second CO ligand.

[†] ³¹P{¹H} NMR (C₆D₆): **3**: δ 593.2, **4**: δ 36.8 and -189.1 (*J*_{PP} 480.3 Hz); **7**: δ -1.1 and -19.7 (*J*_{PP} 38.4 Hz), **9**: δ 451.2; **10**: δ 400.3 and -131.1 (AX, *J* 483.7 Hz).

¹³C{¹H} NMR (50 MHz, C₆D₆): **3**: δ 215.2 (d, *J* 3.6 Hz, CO), 211.2 (d, *J* 110.9 Hz, P=C) 88.5 (d, *J* 4.3 Hz, C₅H₅), 3.9 (d, *J* 12.4 Hz, SiMe), 3.5 (d, *J* 6.5 Hz, SiMe), **7**: δ 220.4 (d, *J* 5.3 Hz, CO), 218.7 (d, *J* 5.5 Hz, CO), 161.7 (d, *J* 3.0 Hz, ring CO), 131.3 (dd, *J* 10.8 and 8.8 Hz, =CSiMe₃), 115.7 (d, *J* 3.8 Hz, =COSiMe₃), 81.3 (s, Cp), 78.5 (d, *J* 1.0 Hz Cp), 22.6 [d, *J* 6.0 Hz, C(SiMe₃)₂] 2.4 (d, *J* 11.4 Hz, SiMe), 1.8 (s, SiMe), 1.1 (d, *J* 8.9 Hz, SiMe); **10**: δ 211.4 (d, *J* 3.2 Hz, CO), 155.4 (dd, *J* 57.5 and 12.5 Hz, P=C), 41.8 (d, *J* 90.5 Hz, P-C), 40.1 (d, *J* 92.1 Hz, P-C), 6.4 (s, Me), 3.8 (d, *J* 9.5 Hz, CH₂), 2.9 (dd, *J* 2.5 and 2.4 Hz, SiMe), 2.2 (dd, *J* 4.8 and 4.7 Hz, SiMe), 1.4 (s, SiMe), 1.1 (d, *J* 7.5 Hz, SiMe).

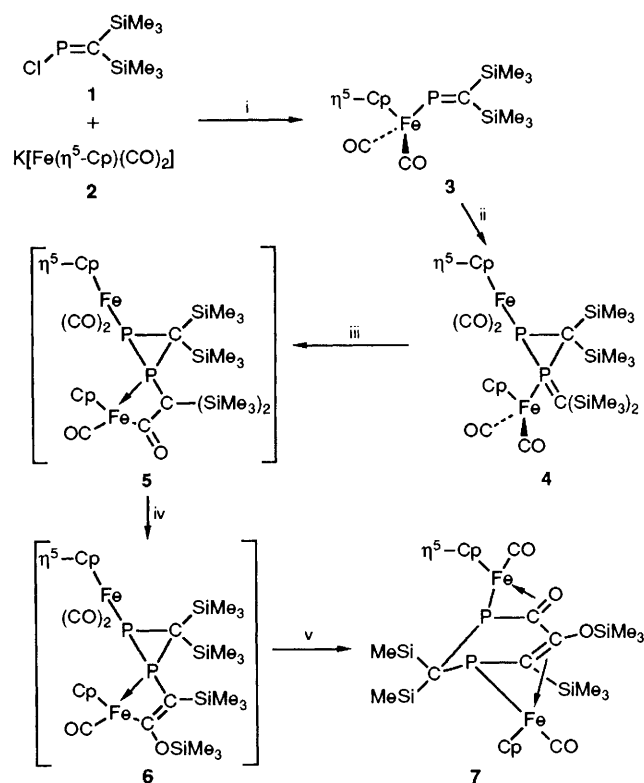
¹H NMR (200 MHz, C₆D₆): **3**: δ 4.19 (d, *J* 2.3 Hz, 5H, C₅H₅), 0.57 (s, 9H, SiMe), 0.42 (d, *J* 2.6 Hz, 9H, SiMe); **7**: δ 4.13 (s, 5H, Cp), 3.89 (br, 5H, Cp), 0.35 (d, *J* 2.0 Hz, 18H, SiMe), 0.28 (s, 9H, SiMe), 0.10 (s, 9H, SiMe); **10**: δ 0.36 (d, *J* 1.8 Hz, 9H, SiMe), 0.35 (d, *J* 9.3 Hz, 2H, CH₂), 0.28 (s, 3H, Me), 0.27 (d, ~1.0 Hz, 9H, SiMe), 0.21 (d, *J* 3.3 Hz, 18H, SiMe), 0.24 (dd, *J* 4.6 and 0.6 Hz, 1H, P-CH).

MS (50 eV; 700 μA): **7**: *m/z* (%) 732 (11) [M⁺], 704 (44) [M⁺-CO], 676 (1) [M⁺-2CO], 639 (30) [M⁺-CO-C₅H₅], 147 (100) [Me₃SiO-SiMe₃], 73 (100) [SiMe₃], **10**: *m/z* (%) 700 (1) [M⁺], 658 (1) [M⁺-C₃H₆], 588 (3) [M⁺-4CO], 546 (2) [M⁺-4CO-C₃H₆], 462 (6) [M⁺-Fe(CO)₅-C₃H₆], 434 (66) [M⁺-Fe(CO)₅-C₃H₆-CO], 346 (22) [M⁺-Fe(CO)₅-C₃H₆-CO-SiMe₄], 73 (100) [SiMe₃].

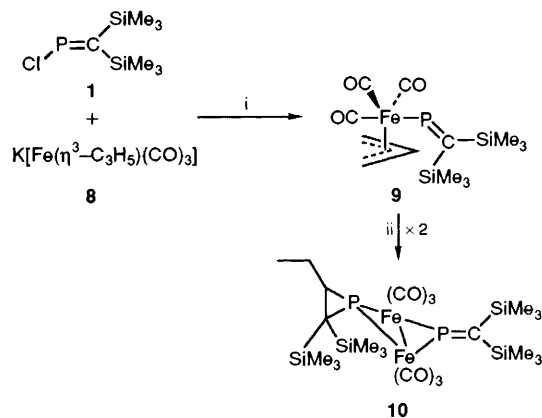
IR (pentane): ν(CO)/cm⁻¹ **7**: 1955s, 1932vs, 1785s, **10**: 2026vs, 1987vs, 1971s.

Elemental analyses: **7**, Found: C, 44.9; H, 6.1; C₂₈H₄₆Fe₂O₄P₂Si₄ requires C, 45.9; H, 6.3%. **10**, Found: C, 40.0; H, 6.2; C₂₃H₄₂Fe₂O₆P₂Si₄ requires C, 39.4; H, 6.0%.

Support for this proposal is gained from comparison with similar pathways observed during the rearrangements of bis(methylene)phosphorane⁻⁵ and diphosphaallylic-iron complexes.⁶ However, ³¹P NMR spectroscopic evidence could be obtained only for the first intermediate, assumed to be a three-membered ring system containing one P^{III} and one P^V phosphorus atom.



Scheme 1 Conditions: i, thf, 2 h, -70 °C; ii-v, thf, 10 days, 20 °C or 1,2-dimethoxyethane, 30 days, 20 °C, 46% of **7**



Scheme 2 Conditions: i, thf, 1 h, -70 °C; ii, 0.5 h, -30 °C or 3 h, -70 °C → 20 °C, -C₃H₄, 51% of **10**

The chemical shift values of $\delta -1.1$ and -19.7 for **7** and the small coupling constant (J_{PP} 38.4 Hz) are clearly indicative of a diphosphacyclohexenone derivative.⁷ The presence of a C=C and a C=O double bond is indicated by the characteristic low-field ¹³C resonances and the inequivalence of the four trimethylsilyl substituents in both ¹³C and ¹H NMR spectra.† Furthermore, strong support for this interpretation is provided by the IR and high resolution mass spectroscopic data, which reveal three different ligation modes of the carbonyl groups: two terminal, metal-bonded groups and the incorporation of the other CO substituents in the diphosphahexene ligand in two different ways.

The reaction of **1** with $K[Fe(\eta-C_3H_5)(CO)_3]$ was performed analogously and furnished products **9** and **10**, respectively.

Owing to the proposed decreased thermal stability when a sterically less hindered organometallic precursor is used, the second iron complex **9** could only be detected by ³¹P NMR spectroscopy. Nevertheless, the presence of the metallo-methylene-phosphane intermediate **9** may be readily deduced from the deshielded resonance of the methylenephosphane moiety.

The formation of **10** can formally be viewed as a dimerization of the metallo-methylenephosphane **9**, which proceeded within 30 min at -30 °C with extrusion of C_3H_4 . Valuable information on the structure of **10** was gained from the ³¹P{¹H} and ¹³C NMR, and high resolution mass spectra. The presence of a dinuclear complex with a bridging $(CO)_3Fe-Fe(CO)_3$ fragment and two η^2 coordinated phosphorus atoms was apparent from the spectroscopic data.† The low-field resonance (δ 400.3) of the AX pattern was attributed to the methylenephosphane moiety and the shielded resonance ($\delta -131.1$) to the phosphirane phosphorus atom.

Further efforts to achieve full characterization of the intermediates are in progress, as are further studies concerning the reactivity of metallo-methylenephosphanes.

We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the SERC and the British-German Academic Research Collaboration Programme (H.J.M.)

Received, 20th August 1991; Com. 1/04365J

References

- 1 J. F. Nixon, *Chem. Rev.*, 1988, **88**, 1327; R. Appel, in *Multiple Bonding and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Thieme Verlag, Berlin, 1990, p. 157.
- 2 D. Gudat and E. Niecke, *J. Chem. Soc., Chem. Commun.*, 1987, 10; D. Gudat, E. Niecke, W. Malisch, U. Hofmockel, S. Quashie and A. H. Cowley, *Organometallics*, 1986, **5**, 593; H. J. Metternich, E. Niecke, D. Gudat, P. Wenderoth, W. Malisch and U. Hofmockel, *Chem. Ber.*, submitted.
- 3 D. Gudat, E. Niecke, W. Malisch, U. Hofmockel, S. Quashie, A. H. Cowley, A. M. Arif, B. Krebs and M. Dartmann, *J. Chem. Soc., Chem. Commun.*, 1985, 1687; J. Hein, E. Niecke and M. Nieger, *Organometallics*, 1989, **8**, 2290; A. H. Cowley, N. C. Norman and S. Quashie, *J. Am. Chem. Soc.*, 1984, **106**, 5007.
- 4 R. Appel and A. Westerhaus, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 556.
- 5 H. J. Metternich and E. Niecke, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 313.
- 6 E. Niecke and D. Schmidt, *J. Chem. Soc., Chem. Commun.*, 1991, 1659.
- 7 M. J. Gallagher, in *Phosphorus-13 NMR Spectroscopy in Stereochemical Analysis*, ed. J. G. Verkade and L. D. Louis, VCH Publishers, Weinheim, 1987, p. 297.