

Stabilization of 7-Phosphanorbornadienes by Complexation; X-Ray Crystal Structure of 2,3-Bis(methoxycarbonyl)-5,6-dimethyl-7-phenyl-7-phosphanorbornadiene(pentacarbonyl)-chromium

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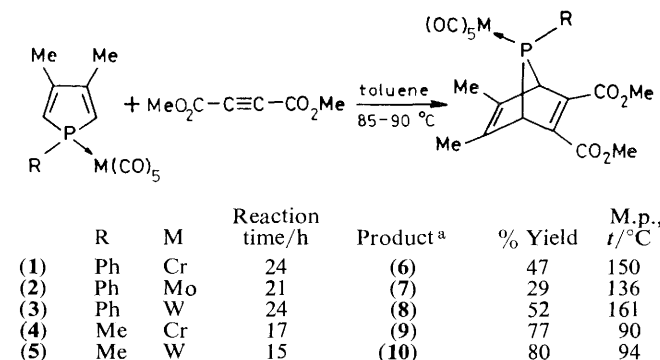
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The reaction of dimethyl acetylenedicarboxylate with LM(CO)₅ complexes (L = 1-substituted-3,4-dimethylphosphole; M = Cr, Mo, W) provides an easy access to stable 7-phosphanorbornadiene complexes, the X-ray crystal structure of one of which is reported; the ³¹P resonance of these species appears at very low field (ca. 200—260 p.p.m.) and mass spectral and structural data suggest that they may be efficient generators for the still unknown terminal phosphinidene complexes.

The recently discovered 7-phosphanorbornenes^{1,2} display several unusual properties, *e.g.*, a ³¹P resonance at very low field for a phosphine, an easy *syn* to *anti* isomerization at phosphorus in protic solvents,^{2,3} and an easy thermal decomposition to yield phosphinidenes through a retro-Diels-Alder reaction. Thus, it was tempting to try to synthesize the still unknown 7-phosphanorbornadienes which might display the same unusual properties to an even greater extent. The obvious route was to condense a reactive acetylenic dienophile, such as dimethyl acetylenedicarboxylate, with a monomeric λ⁵-phosphole derivative.⁴ However, this reaction has always led to the loss of the phosphorus bridge in the expected 7-phosphanorbornadienes⁵ and only one 7-phosphanorbornadiene *P*-oxide has been made hitherto by an indirect route.⁶ We have found that it is possible to avoid this loss by using λ³-phosphole, P → M(CO)₅ complexes (M=Cr,Mo,W),⁷ in place of unco-ordinated λ⁵-phosphole derivatives.

The reactions were carried out under argon with a 3-fold excess of acetylenedicarboxylate and the disappearance of the starting complex was monitored by ³¹P n.m.r. spectroscopy. The final complex was purified by chromatography on a silica gel column with toluene. When R=Bu^t, no condensation takes place indicating a significant sensitivity of the reaction to steric hindrance around phosphorus. In connection with this it is interesting to note that, on the basis of the X-ray structural analysis of (6) (see later), the attack of the acetylene takes place exclusively on the less hindered side of the co-ordinated phosphole, *i.e.*, the side of the R group.

We have also attempted this synthesis with P → Fe(CO)₄ complexes but loss of the phosphorus bridge was always observed, suggesting that the M(CO)₅ group plays a very special role in the stabilization of the 7-phosphanorbornadiene



^a δ(³¹P) for toluene solutions in p.p.m. from H₃PO₄; downfield shifts +ve: (6), 262.4; (7), 234.6; (8), 208, ¹J(¹⁸³W-³¹P) 236.8 Hz; (9), 254.3; (10), 199.6, ¹J(¹⁸³W-³¹P) 236.8 Hz.

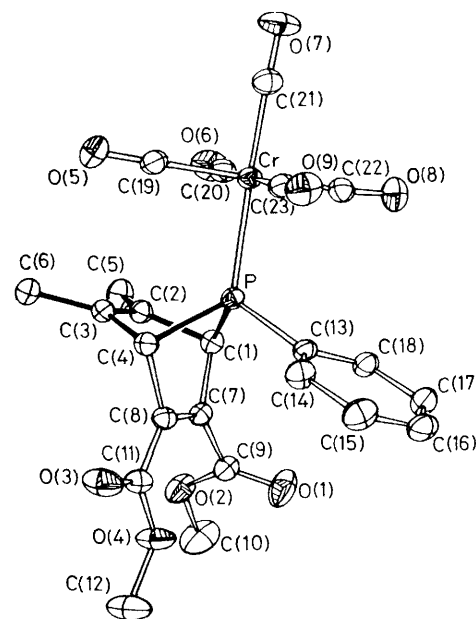
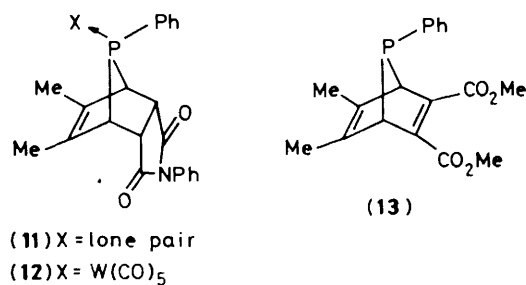


Figure 1. ORTEP drawing (30% probability ellipsoids), showing the atom numbering scheme (hydrogen atoms are omitted). Principal bond distances are Cr—P: 2.347(1), P—C(1): 1.877(3), P—C(4): 1.878(3), P—C(13): 1.822(3), C(1)—C(2): 1.533(4), C(3)—C(4): 1.527(4), C(2)—C(3): 1.337(4), C(1)—C(7): 1.526(4), C(4)—C(8): 1.532(4), C(7)—C(8): 1.337(4) Å. Bond angles C(1)—P—C(4): 79.0(1), P—C(1)—C(2): 97.1(1), P—C(4)—C(3): 97.4(1), C(1)—P—Cr: 122.6(1), C(4)—P—Cr: 123.8(1), P—C(1)—C(7): 100.6(1), P—C(4)—C(8): 100.4(1)°.

skeleton. The ¹H n.m.r. and i.r. data are entirely conventional and need no comment except to note the shielding effect of the *P*-phenyl substituents on the methoxy groups in (6), (7), and (8) [in CDCl₃: δ 3.67 vs. 3.83 in (9) and (10)]. However, the exceptional ³¹P deshielding in all these phosphanorbornadiene complexes deserves some attention. Using the measured co-

ordination chemical shift between (11)² and (12)[†] [$\Delta\delta(^{31}\text{P}) = +31.7$ p.p.m.] which are structurally close to (13) and (8), it is possible to calculate an approximate value for the ³¹P chemical shift of (13). The value thus found [$\delta(^{31}\text{P})$ ca. +176 p.p.m.] falls in the range normally associated with P^{III} compounds. If it is isolable in the free state, (13) will probably have the most deshielded ³¹P resonance ever observed for a phosphine.

The mass spectral data[‡] provide more interesting information. The molybdenum and tungsten complexes (7) and (8) appear to lose the whole PhP-M(CO)₅ unit in the mass spectrometer suggesting that these complexes might be convenient generators for the still unknown terminal phosphinidene complexes. The X-ray crystal structure of complex (6)[§]

[†] Complex (12) was prepared either by allowing phosphine (11) to react with W(CO)₅(THF) at room temperature for 30 min or by allowing complex (3) to react with *N*-phenylmaleimide in refluxing dichloromethane for 21 h; yield ca. 70%, m.p. 246 °C, $\delta(^{31}\text{P})$ (CH₂Cl₂): +77.2 p.p.m.

[‡] (7) (70 eV, 180 °C, ⁹⁸Mo) *m/z* 568 (*M*, 1%); 484 (*M* - 3CO, 2.4%); 428 (*M* - 5CO, 4.3%); 346 [PhP-Mo(CO)₅, 1%]; 318 (346 - CO, 3.9%); 290 (346 - 2CO, 3%); 262 (346 - 3CO, 8%) 234 (346 - 4CO, 3.3%); 222 [*M* - PhP-Mo(CO)₅, 37%]; 206 (346 - 5CO, 4.5%); 191 (222 - OMe, 100%). (8) (70 eV, 160 °C, ¹⁸⁴W) *m/z* 654 (*M*, 1.3%); 570 (*M* - 3CO, 0.6%); 542 (*M* - 4CO, 2.3%); 514 (*M* - 5CO, 1.4%); 432 [PhP-W(CO)₅, 7%]; 404 (432 - CO, 26%); 376 (432 - 2CO, 5%); 348 (432 - 3CO, 29%); 320 (432 - 4CO, 12%); 292 (432 - 5CO, 15%); 222 [*M* - PhP - W(CO)₅, 12%]; 191 (222 - OMe, 100%).

[§] Crystal data for (6): C₂₃H₁₉CrPO₉, *M* = 522.37, monoclinic, space group *P*2₁/*n*, *a* = 20.821(8), *b* = 9.094(3), *c* = 13.401(5) Å, β = 103.53(2)°, *U* = 2467 Å³, *D*_c = 1.40 g cm⁻³, *Z* = 4. A total of 2691 observed reflexions [*I* > 3σ(*I*)] were used out of 3631 collected with a Philips PW1100/16 diffractometer employing the $\theta - 2\theta$ flying step-scan technique (θ_{max} = 57°) with graphite monochromated Cu-K_α radiation. Intensities were corrected for Lorentz polarisation and absorption factors. The structure was solved by the heavy atom method and refined by full-matrix least-squares techniques to give a final unweighted *R*-factor of 0.038. The atomic co-ordinates of this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication No. SUP. 23333 (13 pp.) from the British Library. For details see Notice to Authors No. 7, *J. Chem. Soc., Dalton or Perkin Trans.*, Index issues.

(Figure 1) strongly supports this idea. The intracyclic P-C bond lengths are significantly longer than usual [mean value: 1.877(2) vs. 1.84 Å for the sum of the covalent radii of P and C, and 1.822(3) Å for the P-Ph bond length] and the structure appears to be very strained [C-P-C intracyclic angle = 79.0(1) vs. ca. 100° in normal phosphine complexes]. We are currently trying to check this possibility by studying the thermal and photochemical decomposition of these species.

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References

- 1 L. D. Quin and K. A. Mesch, *J. Chem. Soc., Chem. Commun.*, 1980, 959.
- 2 F. Mathey and F. Mercier, *Tetrahedron Lett.*, 1981, 22, 319.
- 3 K. A. Mesch and L. D. Quin, *Tetrahedron Lett.*, 1980, 21, 4791.
- 4 The use of λ³-phosphole instead of λ³-phosphole derivatives is necessary in order to avoid the reaction of the electrophilic acetylenic dienophile at the phosphorus lone pair, see: A. N. Hughes and S. Uaboonkul, *Tetrahedron*, 1968, 24, 3437; N. E. Waite and J. C. Tebby, *J. Chem. Soc. C*, 1970, 386; D. G. Holah, A. N. Hughes, and D. Kleemola, *J. Heterocycl. Chem.*, 1978, 15, 1319.
- 5 I. G. M. Campbell, R. C. Cookson, M. B. Hocking, and A. N. Hughes, *J. Chem. Soc.*, 1965, 2184; F. B. Clarke and F. H. Westheimer, *J. Am. Chem. Soc.*, 1971, 93, 4541; Y. Kashman, I. Wagenstein, and A. Rudi, *Tetrahedron*, 1976, 32, 2427. However, Stille has been able to condense benzyne with penta-phenylphosphole oxide without losing the phosphorus bridge: J. K. Stille, J. L. Eichelberger, J. Higgins, and M. E. Freeburger, *J. Am. Chem. Soc.*, 1972, 94, 4761. The benzannellation may have a stabilizing effect on the norbornadiene skeleton in that case.
- 6 U. Schmidt, I. Boie, C. Osterroht, R. Schröer, and H. F. Grutzmacher, *Chem. Ber.*, 1968, 101, 1381.
- 7 Complexes (1), (3), (4), and (5) were made by allowing Cr(CO)₆(THF) or W(CO)₅(THF) (THF = tetrahydrofuran) to react with the appropriate phospholes at room temperature in THF for 30 min. Complex (2) was made by heating a mixture of phosphole, Mo(CO)₆, and Me₃NO in boiling CH₂Cl₂ for 6 h. Complexes (1), (2), and (3) have been already described: C. C. Santini, J. Fischer, F. Mathey, and A. Mitschler, *J. Am. Chem. Soc.*, 1980, 102, 5809.