# *Ortho*-Phosphination of azobenzene by terminal phosphinidene complexes

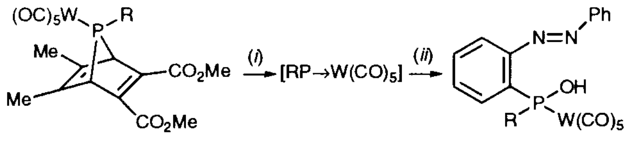
**Ngoc Hoa Tran Huy, Louis Ricard and François Mathey***

*Laboratoire 'Hétéroéléments et Coordination' URA CNRS 1499, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France*

Transient terminal phosphinidene complexes $[\mathrm{RP} \rightarrow \mathrm{W(CO)_5}]$ (R = Ph or Me) as generated from the appropriate 7-phosphanorbornadiene precursors, insert at 110 °C into the *ortho*-C—H bonds of azobenzene.

The insertion of electrophilic terminal phosphinidene complexes [RP—M] $\{\mathrm{M = Fe(CO)_4}$, $[\mathrm{Cp^*Fe(CO)_2}]^+$, $\mathrm{Mo(CO)_5}$ or $\mathrm{W(CO)_5}\}$ into C—H bonds has only been observed in a few cases until now. The two initially reported reactions are intramolecular.[1,2] Later, intermolecular insertions were described with ferrocene[3] and methylketones.[4] During a systematic investigation of the reactions of $[\mathrm{RP—W(CO)_5}]$ with hetero double bonds,[5] we have found a related reaction involving azobenzene. Our experiments were carried out with transient $[\mathrm{PhP \rightarrow W(CO)_5}]$ and $[\mathrm{MeP \rightarrow W(CO)_5}]$ as generated from the appropriate 7-phosphanorbornadiene precursors at 110 °C.[6] The reaction with azobenzene essentially yields *ortho*-phosphino derivatives.†

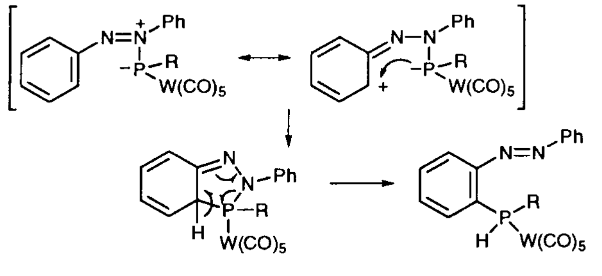
The structure of **3** was established by X-ray analysis (Fig. 1).‡ The proposed mechanism is depicted in Scheme 2.



**1** R = Ph
**2** R = Me

**3** R = Ph (55%)
**4** R = Me (40%)

**Scheme 1** Reagents and conditions: (*i*) toluene, 110 °C, 8 h; (*ii*) $\mathrm{Ph_2N_2}$ in excess (2 : 1)



**Scheme 2** Proposed mechanism for the *ortho*-phosphination of azobenzene

We suspect the initial formation of a zwitterionic adduct between the diazene and the phosphinidene. A similar adduct has been proposed as the initial step of the reaction between benzophenone and phosphinidene complexes.[7,8] In such a way, the phosphinidene phosphorus is placed close to the aromatic *ortho*-C—H bond. This favours the intramolecular attack of P at the aromatic carbon. The cleavage of the weak P—N bond completes the process. Oxidative hydrolysis by $\mathrm{Ph_2N_2 + H_2O}$ transforms the resulting P—H into P—OH derivatives : P—H → P—NPh—NHPh → P—OH. This last point has been checked as shown in Scheme 3.

The formation of **7** was monitored by $^{31}$P NMR spectroscopy [$\delta^{31}$P (**7**) + 73.7]. The methanolysis product **8** was completely characterized as usual.† The decomplexation of compounds such as **8** is probably possible using the classical

---

† Selected spectroscopic data for **3**: purified by chromatography on silica gel (hexane–$\mathrm{CH_2Cl_2}$, 10 : 1), 55% yield; $^{31}$P NMR ($\mathrm{CDCl_3}$): $\delta + 110.6$ [$^1J(^{31}\mathrm{P}—^{183}\mathrm{W})$ 287 Hz]; $^{13}$C NMR ($\mathrm{CDCl_3}$): $\delta$ 138.09 [d, $^1J_{\mathrm{C\text{-}P}}$ 30.2, P-*C*(Ph)], 143.65 [d, $^1J_{\mathrm{C\text{-}P}}$ 41.0, P-*C*(Ph)], 152.25 (d, $^2J_{\mathrm{C\text{-}P}}$ 19.2, C—N), 196.63 (d, $^2J_{\mathrm{C\text{-}P}}$ 8.9, W—CO *cis*), 199.97 (d, $^2J_{\mathrm{C\text{-}P}}$ 26.9 Hz, W—CO *trans*); *m*/*z* ($^{184}$W) 630 ($\mathrm{M^+}$, 0.7%), 614 ($\mathrm{M^+}$ − [O], 28), 546 ($\mathrm{M^+}$ − 3CO, 7), 518 ($\mathrm{M^+}$ − 4CO, 10), 490 ($\mathrm{M^+}$ − 5CO, 29), 474 ($\mathrm{M^+}$ − 5CO − [O], 100).

For **4**: 40% yield; $^{31}$P NMR ($\mathrm{CDCl_3}$): $\delta + 109.1$ [$^1J(^{31}\mathrm{P}—^{183}\mathrm{W})$ 279 Hz]; $^1$H NMR ($\mathrm{CDCl_3}$): $\delta$ 2.30 ($^2J_{\mathrm{H\text{-}P}}$ 6.2 Hz); $^{13}$C NMR ($\mathrm{CDCl_3}$): $\delta$ 29.19 (d, $^1J_{\mathrm{C\text{-}P}}$ 27.3 Hz, Me), 141.03 [d, $^1J_{\mathrm{C\text{-}P}}$ 28.6, P-*C*(Ph)], 152.07 (d, $^2J_{\mathrm{C\text{-}P}}$ 15.5, C—N), 196.81 (d, $^2J_{\mathrm{C\text{-}P}}$ 8.0 Hz, W—CO *cis*), 200.08 (d, $^2J_{\mathrm{C\text{-}P}}$ 24.5 Hz, W—CO *trans*); *m*/*z* ($^{184}$W) 568 ($\mathrm{M^+}$, 0.7%), 552 ($\mathrm{M^+}$ − [O], 12.7), 512 ($\mathrm{M^+}$ − 2CO, 42), 456 ($\mathrm{M^+}$ − 4CO, 95), 428 ($\mathrm{M^+}$ − 5CO, 75), 411 ($\mathrm{M^+}$ − 5CO − [OH], 100).

For **8**: 35% yield; $^{31}$P NMR ($\mathrm{CDCl_3}$): $\delta + 121.7$ [$^1J(^{31}\mathrm{P}—^{183}\mathrm{W})$ 287 Hz]; $^1$H NMR ($\mathrm{CDCl_3}$): $\delta$ 3.40 (d, $^3J_{\mathrm{H\text{-}P}}$ 12.2 Hz, OMe); $^{13}$C NMR ($\mathrm{CDCl_3}$): $\delta$ 54.65 (d, $^2J_{\mathrm{C\text{-}P}}$ 7.7 Hz, OMe), 135.79 [d, $^1J_{\mathrm{C\text{-}P}}$ 38.1, P-*C*(Ph)], 138.52 [d, $^1J_{\mathrm{C\text{-}P}}$ 41.0, P-*C*(Ph)], 152.74 (d, $^2J_{\mathrm{C\text{-}P}}$ 22.7, C—N), 196.98 (d, $^2J_{\mathrm{C\text{-}P}}$ 7.6, W—CO *cis*), 200.17 (d, $^2J_{\mathrm{C\text{-}P}}$ 26.1, W—CO *trans*); *m*/*z* ($^{184}$W) 644 ($\mathrm{M^+}$, 1%), 588 ($\mathrm{M^+}$ − 2CO, 44), 532 ($\mathrm{M^+}$ − 4CO, 36), 504 ($\mathrm{M^+}$ − 5CO, 100).

‡ X-Ray structure determination for **3**: Crystals of **3**, $\mathrm{C_{23}H_{15}N_2O_6PW \cdot 0.5C_6H_{12}}$ were grown from a dichloromethane–hexane solution of the compound. Data were collected at 123 ± 0.5 K on an Enraf Nonius CAD4 diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The crystal structure was solved and refined using the Enraf Nonius MOLEN package. The compound crystallises in space group $P\bar{1}$ (no. 2), $a = 8.138(1)$, $b = 12.478(1)$, $c = 12.481(1)$ Å, $\alpha = 102.64(1)$, $\beta = 90.94(1)$, $\gamma = 102.69(2)°$; $U = 1203.68(45)$ Å$^3$; $Z = 2$; $d_{\mathrm{calc}} = 1.855$ g cm$^{-3}$; $\mu = 50.1$ cm$^{-1}$; $F(000) = 656$. A total of 3677 unique reflections were recorded in the range $2° \leqslant 2\theta \leqslant 46.8°$ of which 459 were considered as unobserved $[F^2 < 3.0\sigma(F^2)]$, leaving 3218 for solution and refinement. Direct methods (SIR92) yielded a solution for all atoms. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic thermal parameters for all other atoms. A non-Poisson weighting scheme was applied with a *p* factor equal to 0.08. The final agreement factors were $R = 0.031$, $R_w = 0.042$, goodness-of-fit = 1.01. The hexane solvate [atoms C(26)–C(29)] is located on a symmetry center and is highly disordered.

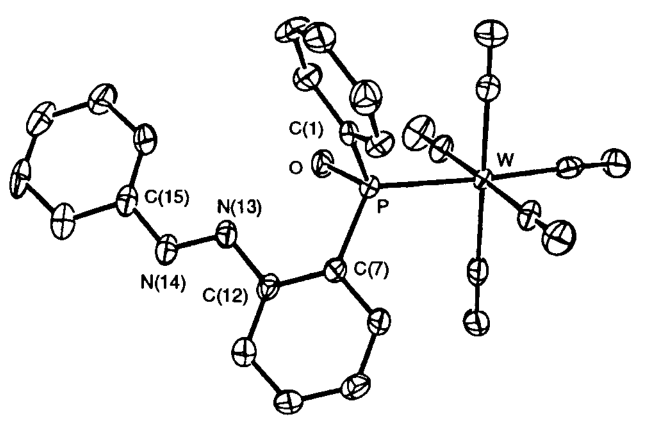
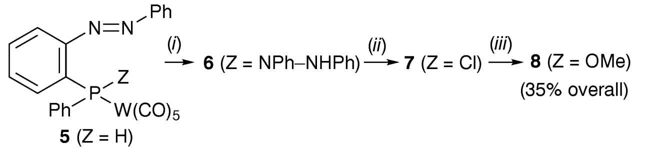


**Fig. 1** Crystal structure of **3**. Significant bond distances (Å) and angles (°): W—P 2.485(1), P—O 1.602(4), P—C(1) 1.820(5), P—C(7) 1.846(5), C(7)—C(12) 1.394(7), C(12)—N(13) 1.445(6), N(13)—N(14) 1.248(6), N(14)—C(15) 1.415(7); W—P—O 110.5(2), W—P—C(1) 114.3(2), W—P—C(7) 119.9(2), O—P—C(1) 104.1(2), O—P—C(7) 104.2(2), C(1)—P—C(7) 102.2(2), P—C(7)—C(12) 124.2(4), C(7)—C(12)—N(13) 116.7(4), C(12)—N(13)—N(14) 114.9(4), N(13)—N(14)—C(15) 115.6(5)



**Scheme 3** Reagents and conditions: (*i*) $Ph_2N_2$ ; (*ii*) dry HCl in $Et_2O$; (*iii*) MeOH in excess

techniques.[9] The rich photochemistry of the azo group[10] suggests that the resulting original *P*,*N*-bidentate ligands might be used with some profit in transition-metal chemistry.

CCDC reference number 440/016.

## References

1 H. Nakazawa, W. E. Burho, G. Bertrand and J. A. Gladysz, *Inorg. Chem.*, 1984, **23**, 3431.
2 D. H. Champion and A. H. Cowley, *Polyhedron*, 1985, **4**, 1791.
3 J. Svara and F. Mathey, *Organometallics*, 1986, **5**, 1159.
4 Y. Inubushi, N. H. Tran Huy and F. Mathey, *Chem. Commun.*, 1996, 1903.
5 Reviews on the chemistry of terminal phosphinidene complexes: F. Mathey, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 275; A. H. Cowley and A. R. Barron, *Acc. Chem. Res.*, 1988, **21**, 81; F. Mathey, *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, eds. M. Regitz and O. J. Scherer, Thieme, Stuttgart, 1990, p. 38; K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester, in the press.
6 A. Marinetti, F. Mathey, J. Fischer and A. Mitschler, *J. Chem. Soc., Chem. Commun.*, 1982, 667; A. Marinetti, F. Mathey, J. Fischer and A. Mitschler, *J. Am. Chem. Soc.*, 1982, **104**, 4484.
7 R. Streubel, A. Ostrowski, H. Wilkens, F. Ruthe, J. Jeske and P. G. Jones, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 378.
8 Y. Inubushi, N. H. Tran Huy, L. Ricard and F. Mathey, *J. Organomet. Chem.*, 1997, **533**, 83.
9 Some examples: A. Marinetti, F. Mathey, J. Fischer and A. Mitschler, *J. Chem. Soc., Chem. Commun.*, 1984, 45; A. Espinosa-Ferao, B. Deschamps and F. Mathey, *Bull. Soc. Chim. Fr.*, 1993, **130**, 695; S. Krill, B. Wang, J-T. Hung, C. J. Horan, G. M. Gray and K. Lammertsma, *J. Am. Chem. Soc.*, 1997, **119**, 8432.
10 See for example: W. Adam, J. N. Moorthy, W. M. Nau and J. C. Scaiano, *J. Am. Chem. Soc.*, 1997, **119**, 6749, and references therein.

*Received* 18*th December* 1997; *Paper* 7/09097H