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Using the 1,2-Dihydro-1,2-diphosphinine Ring as a Template for the Synthesis of New Bicyclic Structures and New Trans-chelating Bis-phosphines

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ABSTRACT: *The 1,2-dihydro-1,2-diphosphinine decacarbonylditungsten complex* **1** *has been used as a synthetic equivalent of the corresponding 1,2-dianion* **2**. *These two 1,2-positions can be linked by a* $(CH_2)_4$ *bridge to yield a [4.4.0] bicyclic structure* **6** *whose identity has been confirmed by X-ray crystal structure analysis. Alternatively, two ω-iodohexyl chains can be grafted onto these positions and the resulting diiodo derivative* **9** *transformed into a long-chain bis-phosphine* **10** *by reaction with lithium diphenylphosphide. This bis-phosphine gives a chelate complex with* $PdCl_2$ *whose trans-stereochemistry was established by X-ray crystal structure analysis.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:44–48, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20073

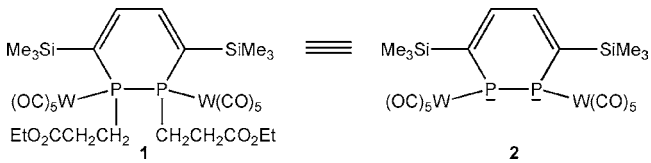
INTRODUCTION

In a preceding work, we proposed an easy access to the almost unknown 1,2-dihydro-1,2-diphosphinine ring system by head-to-head dimerization of phosphirenes and described some of its chemistry [1,2]. Hereafter, we show how it is possible to take advantage of this chemistry to build original bicyclic structures and to prepare bis-phosphines whose geometry favors the *trans*-chelation of square planar d^8 metals.

RESULTS AND DISCUSSION

Our experiments were carried out with compound **1** which is synthetically equivalent to dianion **2** via a stepwise base-induced dealkylation (see Scheme 1).

The reaction of **1** with potassium *tert*-butylate in THF affords the monoanion **3** that smoothly reacts with 1,4-diiodobutane to give the iodobutylated product **4**. The subsequent treatment of **4** by KO*t*-Bu produces the monoanion **5** which spontaneously



SCHEME 1

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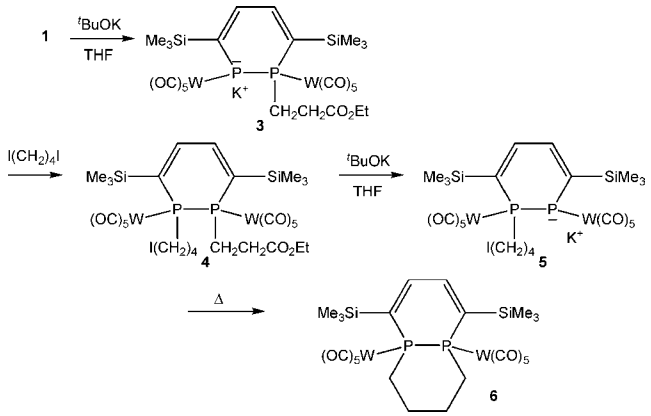
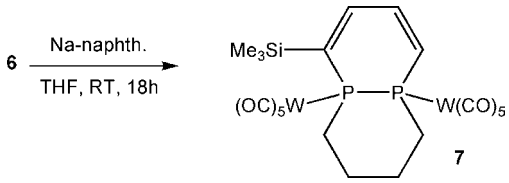
cyclizes to give the original bicyclic product **6** (Eq. (1)).



(1)

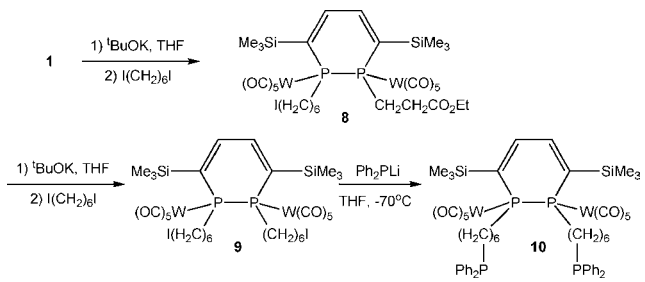
The structure of **6** was investigated by X-ray analysis (Fig. 1). The saturated six-membered ring adopts the usual chair conformation, and the two complexing groups minimize their steric repulsion by a *trans*-diaxial disposition. The diequatorial unsaturated ring is heavily distorted. The sterically protected P–P bond is rather short at 2.186(1) Å. As a result, this bond shows an extraordinary resistance toward cleavage. As an example, the reaction of **6** with naphthalene-sodium leads to the loss of one trimethylsilyl substituent (Eq. (2)).



(2)

The ^{31}P NMR spectrum of **7** ($CDCl_3$) displays two resonances at −9.9 and −30.3 ppm with a small coupling of 84.6 Hz. The structure of **7** with its *trans* stereochemistry at the P–P subunit was established by X-ray analysis and is not reported here because it is very similar to that of **6**. If we admit that the dependence of the $^1J_{P\text{-}P}$ coupling on the lone pair–P–P–lone pair dihedral angle for free diphosphines [3] remains valid for their P-$W(CO)_5$ complexes, then this small value is easily explained by the value of the W–P–P–W dihedral angle in **7** (43°). In the other structurally characterized product of the series [1], the observed stereochemistry is *cis* and the magnitude of the P–P coupling is substantially higher. In fact, the initial dimerization of phosphirenes leads to the *cis*-products. The change of stereochemistry probably takes place during the formation of the delocalized P-anions such as **3** and **5**. Due to the delocalization, these anions are probably close to planar and can react with the electrophiles by their two faces. The favored products correspond to the minimization of the steric repulsion between the two complexing groups.

This chemistry can also serve to prepare original bis-phosphines with interesting coordinating properties. Two ω-iodohexyl chains were first grafted onto the dihydrodiphosphinine ring as shown in Eq. (3). The treatment of the resulting diiodo derivative **9** by lithium diphenylphosphide then afforded the bis-phosphine **10**.



(3)

From a structural standpoint, the bis-phosphine **10** is equivalent to the more classical species Ph_2P-$(CH_2)_{14}$-PPh_2. These long-chain α, ω-bis-phosphines are known to favor the formation of *trans*-square planar complexes with Pd(II) and Pt(II) for

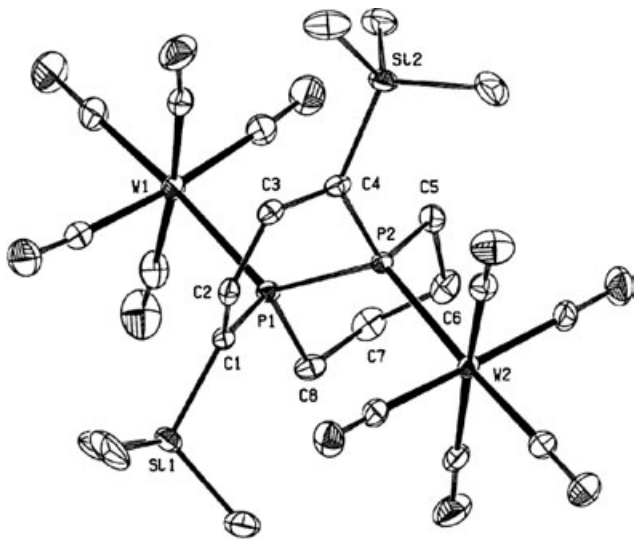
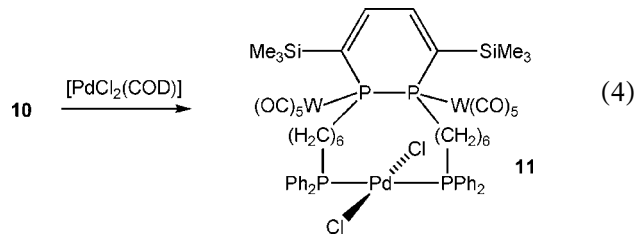


FIGURE 1 ORTEP drawing of one molecule of (**6**). Thermal ellipsoids enclose 50% of the electronic density. Main bond lengths (Å) and angles (°): P(1)–P(2) 2.186(1), P(1)–C(1) 1.818(3), P(1)–C(8) 1.847(3), P(1)–W(1) 2.553(1), P(2)–C(4) 1.828(3), P(2)–C(5) 1.839(3), P(2)–W(2) 2.559(1), C(1)–C(2) 1.358(4), C(2)–C(3) 1.480(4), C(3)–C(4) 1.348(4), C(5)–C(6) 1.539(5), C(6)–C(7) 1.541(5), C(7)–C(8) 1.539(5); C(1)–P(1)–P(2) 94.3(1), P(2)–P(1)–W(1) 124.96(5), C(8)–P(1)–P(2) 96.6(1).

conformational and entropic reasons [4,5]. Thus, the formation of the *trans*-[$PdCl_2$(**10**)] complex (**11**) was not unexpected (Eq. (4)).



(4)

The *trans* stereochemistry of **11** was established by X-ray crystal structure analysis (Fig. 2). Very large residual density appears near both tungsten atoms. Similarly, many thermal parameters are too large, suggesting disorder. Refining the structure with two positions for each W atoms led to 90% occupation of the major sites. Due to a relatively poor crystal quality and low-electron density of the CO groups of the minor sites, disorder could not be completely resolved. Only the major site was considered in completing the refinement. These are the reasons why the numerical parameters are not given in the caption of Fig. 2. We consider however that the *trans* stereochemistry at Pd is established beyond any doubt.

These two series of experiments highlight the flexibility and versatility of the substitution chemistry of 1,2-dihydro-1,2-diphosphinines. Clearly, they can be used as a stable core onto which almost any kind of substituents can be grafted, either identical or different. As such, they can serve, for example, to finetune a bite angle in a transition metal chelate. Recent work has shown that this bite angle can have a profound influence on the catalytic properties of the metallic center [6].

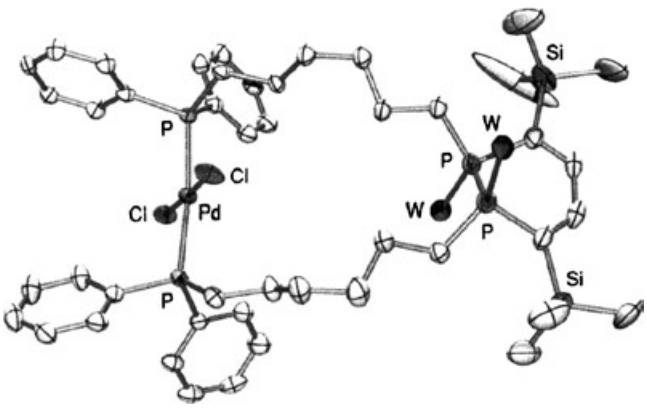


FIGURE 2 Structure of one molecule of (**11**). Hydrogen atoms and carbonyl groups are omitted for clarity.

EXPERIMENTAL

NMR spectra were recorded on a multinuclear Bruker AVANCE 300 MHz spectrometer operating at 300.13 for ^{1}H, 75.47 for ^{13}C, and 121.50 MHz for ^{31}P. Chemical shifts are expressed in parts per million (ppm) downfield from internal tetramethylsilane (^{1}H and ^{13}C) and external 85% aqueous H_3PO_4(^{31}P). Mass spectra were obtained at 70 eV with an HP 5989B spectrometer by the direct inlet method.

Synthesis of Compound **4**

Potassium *tert*-butoxide (70.5 mg, 0.6 mmol) was added to a solution of compound **1** (0.6 g, 0.5 mmol) in THF (5 mL) at 0°C. The solution became red and the formation of the anion **3** was monitored by ^{31}P NMR spectroscopy: AX system: δ_A –30.7, δ_X –115.7, and –116.9 ppm (two diastereomers), J_{AX} = 320 Hz. After 10 min stirring, a THF solution of 1,4-diiodobutane (0.14 mL, 1 mmol) was added and the mixture stirred overnight until it turned yellow. After evaporation of the solvents, the residue was chromatographed on silica gel with 1:1 petroleum ether/dichloromethane as the eluent. Yield of **4** 0.25 g (42%).

^{31}P NMR ($CDCl_3$): δ 2.79 et 1.18, Σ $J_{P\text{-}P}$ = 148 Hz

^{1}H NMR ($CDCl_3$): δ 0.26 (s, 9H, $SiMe_3$), 0.28 (d, 9H, $^4J_{H\text{-}P}$ = 7.6 Hz, $SiMe_3$), 1.16 (t, 3H, CH_3(Et)), 1.4–2.8 (m, 10H, CH_2), 3.14 (m, 2H, CH_2-I) 4.10 (q, 2H, O-CH_2), 6.63 (ABXY, 2H, ring CH).

^{13}C NMR ($CDCl_3$): δ 1.45 (s, $SiMe_3$), 1.73 (s, $SiMe_3$), 4.84 (s, CH_2-I), 14.5 (s, CH_3(Et)), 19.8 (dd, $^1J_{P\text{-}C}$ = 25.7 Hz, $^2J_{P\text{-}C}$ = 9.6 Hz, CH_2-P), 25.8 (dd, $^1J_{P\text{-}C}$ = 25 Hz, $^2J_{P\text{-}C}$ = 9.5 Hz, CH_2-P), 31.05 (d, $^2J_{C\text{-}P}$ = 7.0 Hz, CH_2—C═O), 61.9 (s, O—CH_2), 137.7 (s, C—$SiMe_3$), 139.3 (s, C—$SiMe_3$), 142.8 (d, $^2J_{P\text{-}C}$ = 20.5 Hz, ring CH), 171.0 (d, $^3J_{P\text{-}C}$ = 19.6 Hz, CO_2), 196.3 (d, $^2J_{P\text{-}C}$ = 5.8 Hz, *cis*-CO), 197.8 (d, $^2J_{P\text{-}C}$ = 20.3 Hz, *trans*-CO). MS: *m/z* 1139 (M^+−2CO, 18%), 914 (M^+−10CO, 32%), 544 (100%).

Analysis: calculated for $C_{29}H_{37}O_{12}P_2Si_2IW_2$: C, 29.26; H, 3.13. Found: C, 29.04; H, 3.24.

Synthesis of Compound **6**

Potassium *tert*-butoxide (43.9 mg, 0.38 mmol) was added to a solution of compound **4** (0.38 g, 0.32 mmol) in THF (5 mL) at 0°C. The solution became red. After 10 min stirring at 0°C, the mixture was stirred for 3 h at room temperature until it turned yellow. After evaporation of the solvents, the residue was chromatographed on silica gel with 3:1 petroleum ether/dichloromethane as the eluent. Yield of **6** 0.25 g (pale yellow powder, 81%).

^{31}P NMR ($CDCl_3$): δ −19.27, $^1J_{P\text{-}W} = 166$ Hz, $^2J_{P\text{-}W} = 60$ Hz.

^{1}H NMR ($CDCl_3$): δ 0.202 (s, 18H, $SiMe_3$), 1.8–2.6 (m, 8H, CH_2), 6.48 (ABXY, 2H, ring CH).

^{13}C NMR ($CDCl_3$): δ −0.22 (s, $SiMe_3$), 23.93 (s, CH_2—(CH_2—P)), 25.20 (pseudo-t, $\Sigma J_{P\text{-}C} = 22.2$ Hz, CH_2—P), 142.13 (pseudo-t, $\Sigma J_{P\text{-}C} = 20.0$ Hz, ring CH), 143.37 (s, C—$SiMe_3$). MS: *m/z* 964 (M + 2H, 9%), 739 (M + H − 8CO, 29%), 610 (100%).

Analysis: calculated for $C_{24}H_{28}O_{10}P_2Si_2W_2$: C, 29.96; H, 2.93. Found: C, 29.83; H, 2.91.

Synthesis of Compound **7**

Naphthalene (0.149 g, 2 eq.), then an excess of sodium were added to a solution of **6** (0.6 g) in THF (10 mL). The solution was stirred at room temperature for 18 h. After evaporation of the solvents, the residue was chromatographed on silica gel with 9:1 petroleum ether/dichloromethane as the eluent. Yield of **6** 0.24 g (40%), yield of **7** 0.18 g (32%).

^{31}P NMR ($CDCl_3$): δ (ppm) −9.9 and −30.3, $\Sigma J_{P\text{-}P} = 84.6$ Hz.

^{13}C NMR ($CDCl_3$): δ 0.00 (s, $SiMe_3$), 24.29 (dd, $2 \times CH_2$), 25.24 (dd), 26.83 (dd), 132.30 (d, $J_{P\text{-}C} = 24.1$ Hz, CH), 134.92 (d, $J_{P\text{-}C} = 20.3$ Hz, CH), 141.54 (s, C-$SiMe_3$), 142.57 (d, $^2J_{P\text{-}C} = 15.8$ Hz, βCH).

MS: *m/z* 894 (M + 4H, 10%); 724 (M + 2H − 6CO, 20%); 669 (M + 3H − 8CO, 31%); 539 (M + 3H − 10CO —$SiMe_3$, 100%).

Analysis: calculated for $C_{21}H_{20}O_{10}P_2SiW_2$: C 28.34, H 2.26. Found: C 28.34, H 2.24.

Synthesis of Compound **8**

Potassium *tert*-butoxide (70.5 mg, 0.6 mmol) was added to a solution of compound **1** (0.6 g, 0.5 mmol) in THF (5 mL) at 0°C. The solution turned red. After 10 min stirring, a THF solution of 1,6-diiodohexane (0.19 mL, 1.1 mmol) was added and the mixture stirred overnight until it turned yellow. After evaporation of the solvents, the residue was chromatographed on silica gel with 1:1 hexane/dichloromethane as the eluent. Yield of **8** 0.19 g (29%).

^{31}P NMR ($CDCl_3$): δ 1.83 and 0.33, $\Sigma J_{P\text{-}P} = 149$ Hz.

^{1}H NMR ($CDCl_3$): δ 0.202 (s, 9H, $SiMe_3$), 0.222 (s, 9H, $SiMe_3$), 1.12 (t, 3H, CH_3(Et)), 1.2–2.7 (m, 14H, CH_2), 3.04 (t, 2H, $^3J_{H\text{-}H} = 6.9$ Hz, CH_2—I), 4.03 (q, 2H, O—CH_2), 6.54 (ABXY, 2H, ring CH).

^{13}C NMR ($CDCl_3$): δ 1.79 (d, $^3J_{P\text{-}C} = 6.0$ Hz, $SiMe_3$), 6.88 (s, CH_2—I), 14.5 (s, CH_3(Et)), 25.9 (dd, $^1J_{P\text{-}C} = 24.0$ Hz, $^2J_{P\text{-}C} = 11.0$ Hz, CH_2—P), 61.8 (s, O—CH_2), 138.50, and 138.62 (2s, C—$SiMe_3$), 142.9 (m, ring CH), 171.2 (d, $^3J_{P\text{-}C} = 20.3$ Hz, CO_2), 196.2 (d, $^2J_{P\text{-}C} = 5.3$ Hz, *cis*-CO), 197.8 (d, $^2J_{P\text{-}C} = 16.5$ Hz, *trans*-CO). MS: *m/z* 1167 (M − 2CO, 8%), 941 (M − 10CO, 8%), 543 (100%).

Analysis: calculated for $C_{31}H_{41}O_{12}P_2Si_2IW_2$: C, 30.56; H, 3.39. Found: C, 30.39; H, 3.42.

Synthesis of Compound **9**

Potassium *tert*-butoxide (20 mg, 0.18 mmol) was added to a solution of compound **8** (0.18 g, 0.15 mmol) in THF (3 mL) at 0°C. The solution turned red. After 10 min stirring, a THF solution of 1,6-diiodohexane (0.05 mL, 0.3 mmol) was added and the mixture stirred overnight until it turned yellow. After evaporation of the solvents, the residue was chromatographed on silica gel with 1:1 hexane /dichloromethane as the eluent. Yield of **9** 0.05 g (25%).

^{31}P NMR ($CDCl_3$): δ 0.37, $^1J_{P\text{-}W} = 149$ Hz, $^2J_{P\text{-}W} = 73.6$ Hz.

^{1}H NMR ($CDCl_3$): δ 0.277 (s, 18H, $SiMe_3$), 1.33–2.42 (m, 20H, CH_2), 3.12 (t, 4H, $^3J_{H\text{-}H} = 6.93$ Hz, CH_2—I), 6.61 (ABXY, 2H, ring CH).

^{13}C NMR ($CDCl_3$): δ 1.87 (s, $SiMe_3$), 7.02 (s, CH_2—I), 138.81 (s, C—$SiMe_3$), 142.7 (pseudo-t, $\Sigma J_{P\text{-}C} = 15$ Hz, ring CH), 196.47 (*cis*-CO), 198.13 (*trans*-CO).

MS: *m/z* 1279 (M − 2CO, 3%), 1053 (M − 10CO, 3.5%), 310 (100%). Analysis: calculated for $C_{32}H_{44}O_{10}P_2Si_2I_2W_2$: C, 28.94; H, 3.34. Found: C, 28.83; H, 3.39.

Synthesis of Compound **10**

A solution of lithium diphenylphosphide (2.2 eq.) was added to a solution of compound **9** (0.77 g, 0.57 mmol) in THF (6 mL) at –60°C. The reaction mixture was stirred at −60°C for 30 min, then at RT for 45 min. After evaporation of the solvents, the residue was chromatographed on silica gel with 5:3 hexane /dichloromethane as the eluent. Yield of **10** 0.51 g (yellow oil crystallizing at *ca* 0°C, 58%).

^{31}P NMR ($CDCl_3$)δ -16 (PPh_2), 0.59 (P-W) $J_{P\text{-}W} = 147$ Hz.

^{1}H NMR ($CDCl_3$) δ 0.33 (s, 18H, $SiMe_3$); 1.3, 1.8 (m, 16H, CH_2); 2.24 (m, 8H, Ph_2PCH_2, CH_2P-W); 6.75 (m, 2H, H-ring); 7.31 (m, 12H, Ph meta, para); 7.40 (m, 8H, Ph ortho).

^{13}C NMR ($CDCl_3$) δ 1.76 (s, $SiMe_3$), 128.77, 133.14 (Ph), 133.1 (s), 138.86 (m, C—$SiMe_3$), 142.64 (pseudo-t, $\Sigma J_{P\text{-}C} = 14.8$ Hz, ring CH), 197.24 (CO).

Synthesis of Compound **11**

The complex [$PdCl_2$(COD)] (0.05 g, 1.1 eq.) was added to a solution of diphosphine **10** (0.2 g, 0.14 mmol) in dry dichloromethane (25 mL). The mixture was stirred at RT for 45 min. After evaporation of the solvents, the yellow solid residue was washed with petroleum ether to remove COD. Yield of **11** 0.18 g (80%). Monocrystals were obtained by slow recrystallization from 6:1 hexane/dichloromethane.

^{31}P NMR ($CDCl_3$) δ 0.70 (P-W) and 14.99 (PPh_2).

^{1}H NMR ($CDCl_3$) δ 0.34 (s, 18H, $SiMe_3$); 1.48–1.77 (m, 16H, CH_2); 2.34–2.58 (m, 8H, Ph_2PCH_2, CH_2P-W); 6.73 (m, 2H, H ring); 7.38 (m, 12H, Ph meta, para); 7.59–7.71 (m, 8H, Ph ortho).

^{13}C NMR ($CDCl_3$) δ 0.01 (s, $SiMe_3$); 136.19 (s, C–$SiMe_3$); 140.80 (pseudo-t, $\Sigma\ J_{C\text{-}P} = 15$ Hz, CH ring); 195.02 (cis CO).

Analysis: calculated for $C_{56}H_{64}O_{10}P_4Si_2W_2PdCl_2$: C, 41.46; H, 3.98. Found: C, 41.44; H, 4.02.

X-ray Structure Data

Nonius Kappa CCD diffractometer, ϕ and ω scans, Mo K_α radiation ($\lambda = 0.71073$ Å), graphite monochromator, $T = 150$ K, structure solution with SIR97 [7], refinement against F^2 in SHELXL97 [8] with anisotropic thermal parameters for all non-hydrogen atoms, calculated hydrogen positions with riding isotropic thermal parameters.

Data collection for **6**: yellow plate, 0.18 × 0.18 × 0.12 mm; triclinic, $P-1, a = 9.362(5), b = 10.488(5)$, $c = 18.436(5)$ (Å), $\alpha = 81.090(5)$, $\beta = 76.650(5)$, $\gamma = 67.480(5)$ (°), $V = 1622.5(12)$ Å^3, $Z = 2$, ρ calc = 1.970 g cm^{-3}, $\mu = 7.304$ cm^{-1}, $F(000) = 916$, θ max = 30.03°, HKL ranges: −11 13; −14 14; −25 22, 13,121 data collected, 9427 unique data ($R_{int} = 0.0312$), 8169 data with $I > 2\sigma(I)$,368 parameters refined, GOF(F^2) = 1.049, final R indices ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$): $R_1 = 0.0281$, $wR_2 = 0.0719$, max/min residual electron density 1.959(0.162)/−2.377(0.162) eA^{-3}.

Data collection for **11**: pale yellow block, 0.18 × 0.18 × 0.18 mm; triclinic, $P-1$, $a = 11.4850(10)$, $b = 11.6600(10)$, $c = 27.7610(10)$ (Å), $\alpha = 96.7300(10)$, $\beta = 96.3300(10)$, $\gamma = 110.6000(10)$ (°), $V = 3409.7(4)$ Å^3, $Z = 2$, ρcalc = 1.663 g cm^{-3}, $\mu = 3.962$ cm^{-1}, $F(000) = 1676$, θ max = 27.48°, HKL ranges: −14 14; −14 15; −36 36, 22,672 data collected, 15,081 unique data($R_{int} = 0.0231$), 11,953 data with $I > 2\sigma(I)$,721 parameters refined, GOF(F^2) = 1.063, final R indices: $R_1 = 0.0658$, $wR_2 = 0.1892$, max/min residual electron density 11.406(0.218)/−2.568(0.218) eA^{-3}.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publications no. CCDC-248031 and CCDC-248032. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax (+44)1223-336-033; e-mail : deposit@ccdc.cam.ac.uk).

REFERENCES

[1] Tran Huy, N. H.; Ricard, L.; Mathey, F. Chem Commun 2000, 1137–1138.
[2] Tran Huy, N. H.; Vong, H.; Mathey, F. Organometallics 2002, 21, 336–339.
[3] Duangthai, S.; Webb, G. A. Org Magn Reson 1983, 21, 199–202.
[4] Pryde, A.; Shaw, B. L.; Weeks, B. J Chem Soc, Dalton Trans 1976, 322–327.
[5] Shaw, B. L. J Organomet Chem 1980, 200, 307–318.
[6] Kamer, P. C. J.; Van Leeuwen, P. W. N. M.; Reek, J. N. H. Acc Chem Res 2001, 34, 895–904.
[7] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. SIR97, an integrated package of computer programs for the solution and refinement of crystal structures using single crystal data.
[8] Sheldrick, G. M. SHELXL-97, Universität Göttingen, Göttingen, Germany, 1997.