Palladium Chloride Trimer Complex

A Bowl-Shaped Triarylphosphane with a Large Cone Angle: Synthesis and Crystallographic Analysis of a $[(PdX_2)_3(PR_3)_2]$-Type Complex**

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There has been a growing interest in the molecular design of bulky phosphane ligands,[1] which can facilitate the formation of catalytically active low-coordinate species by their steric properties. The tertiary phosphane complexes of divalent palladium are well recognized as important species because of their effectiveness in organic synthesis and as homogeneous catalysts.[2] Generally, the reactions of tertiary phosphanes with palladium(II) halides produce the 2:1 complexes $[PdX_2(PR_3)_2]$ (X = halide), which may or may not be converted to the 2:2 complexes $[(PdX_2)_2(PR_3)_2]$ upon heating.[3] Although bulky phosphane ligands tend to favor the direct formation of 2:2 complexes,[3] there has been no report of a phosphane ligand bulky enough to form the 2:3 trinuclear complex $[(PdX_2)_3(PR_3)_2]$. Most of the bulky phosphane ligands thus far reported have the substituents in the vicinity of the phosphorus center, which often results in facile intramolecular cyclometallation. For example, trimesitylphosphane ($P(Mes)_3$) reacts with palladium(II) chloride under a wide range of reaction conditions to produce only the cyclometallated dinuclear complex.[4] Although such cyclometallation reactions have attracted much attention in view of the catalytic utility of the resulting metallacycles,[5] they are undesirable when one intends to synthesize a metal complex with the phosphane ligands intact. It is usually difficult, however, to increase the steric bulk of the phosphane ligands without an increase in the steric congestion around the phosphorus center.

In the course of our study on bowl-shaped molecules,[6] we previously designed the triarylmethane,[7a] triarylsilane,[7b] and triarylgermane[7c] derivatives **1**–**3**, in which the radially extended *m*-terphenyl units form a large cavity. It is expected that replacement of the central atom of these molecules by a phosphorus atom will produce very bulky phosphane ligands without severe steric congestion in the vicinity of the phosphorus center. Recently, Tatsumi and co-workers[8] and our group[9] independently reported the synthesis of triarylphosphane TRMP.[10] TRMP was applied to the highly efficient rhodium-catalyzed hydrosilylation of ketones by Tsuji et al.[11] In this communication, we report the synthesis and structure of the first example of the $[(PdX_2)_3(PR_3)_2]$-type trinuclear complex by taking advantage of a novel bowl-shaped phosphane TRIP,[10] in which the methyl groups of TRMP are replaced by isopropyl groups (Figure 1).

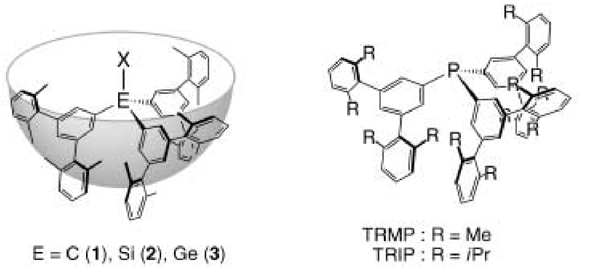
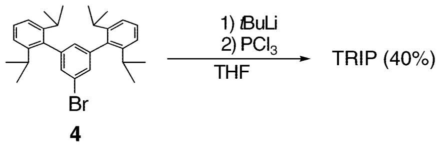


Figure 1. Bowl-shaped molecules that bear *m*-terphenyl units.

TRIP was prepared by lithiation of the corresponding *m*-terphenyl bromide **4**[6e] followed by treatment with PCl_3 (Scheme 1). The ^{31}P NMR spectra ($CDCl_3$) of TRIP showed a signal at $\delta = -6.60$ ppm, which is almost the same as the chemical shifts of TRMP ($\delta = -7.16$ ppm) and triphenylphosphane ($\delta = -6.0$ ppm).[12] X-ray crystallographic analysis established the structure of TRIP (Figure 2),[13] in which the central phosphorus atom is embedded in a bowl-shaped cavity. The space-filling models of the crystal structures of TRMP[9b] and TRIP are shown in Figure 3. Both phosphanes have a diameter of about 16 Å, but the cavity of TRIP is



Scheme 1. Synthesis of TRIP.

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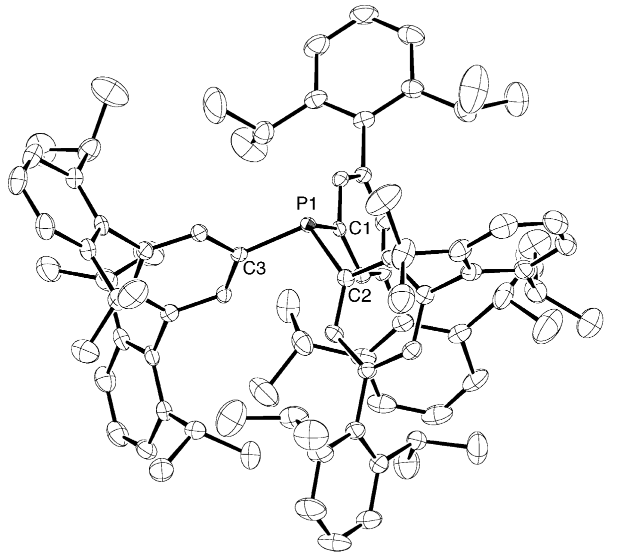
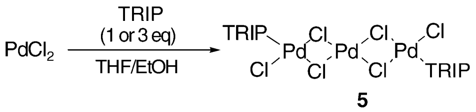


Figure 2. X-ray crystal structure of TRIP (ORTEP drawing, 50% probability). Selected bond lengths [Å] and angles [°]: P1-C1, 1.829(3); P1-C2, 1.830(3); P1-C3, 1.836(3); C1-P1-C2, 101.52(13); C2-P1-C3, 103.48(13); C1-P1-C3, 104.52(13).

deeper than that of TRMP (3.3 Å for TRIP versus 2.1 Å for TRMP). The cone angle of TRIP is estimated to be 206°, which is much larger than those of TRMP (174°),[9b] tri-*t*-butylphosphane (182°)[12] and triphenylphosphane (145°).[12] On the other hand, the averaged C-P-C bond angle of TRIP is 103°, which is almost the same as those of TRMP (102°)[9b] and PPh_3 (103°),[12] in contrast to other bulky phosphanes such as $P(Mes)_3$ (110°).[14] These results indicate that in phosphane TRIP, which bears a dendritic framework, the molecular size is enlarged in comparison with PPh_3 without increasing steric repulsion among the three aryl groups.

The reactions of tertiary phosphanes with divalent palladium chloro salts usually produce the mononuclear complex $[PdCl_2(PR_3)_2]$ or dinuclear complex $[(PdCl_2)_2(PR_3)_2]$, depending on the relative amount of the phosphane ligand. Tatsumi et al. reported that, even in the case of TRMP, the reactions with $PdCl_2$ in the ratio of 1:2 and 1:1 (Pd/ligand) yielded the corresponding mononuclear complex, $[PdCl_2(TRMP)_2]$, and the dinuclear complex, $[(PdCl_2)_2(TRMP)_2]$, respectively.[8a] In contrast, the treatment of $PdCl_2$ with an equimolar amount of TRIP in refluxing ethanol/THF produced the trinuclear palladium(II) chloride complex, $[(PdCl_2)_3(TRIP)_2]$ (**5**), as a single product (Scheme 2). In the ^{31}P NMR spectrum ($CDCl_3$), **5** showed a signal at $\delta = 34.77$ ppm. The structure of **5** was established by X-ray crystallographic analysis (Figure 4).[13]



Scheme 2. Reaction of $PdCl_2$ with TRIP.

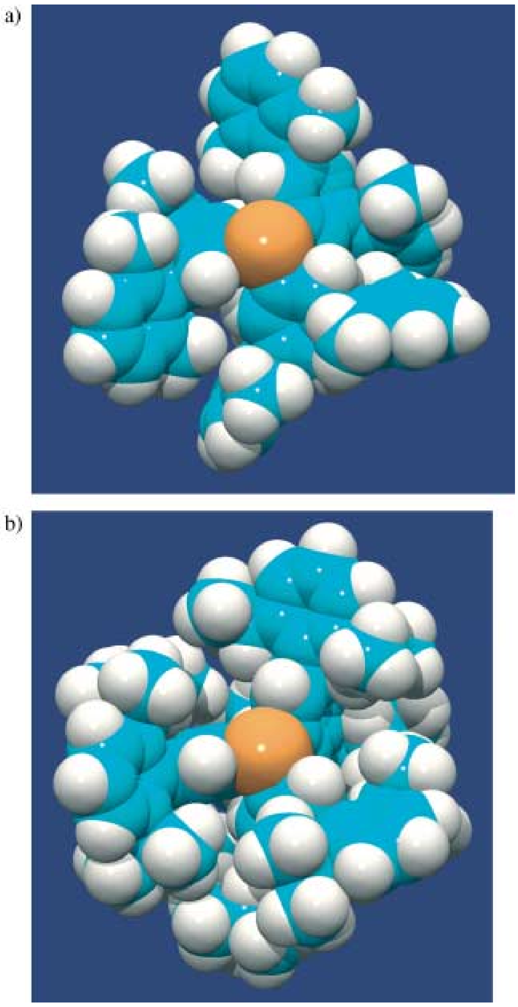


Figure 3. Space-filling models of the crystal structures of a) TRMP and b) TRIP.

The X-ray crystal structure (Figure 4) shows that **5** contains three Pd atoms linked by bridging chloride ligands with the Pd2 atom residing at a crystallographic inversion center. It is known that $PdCl_2$ has a polymeric structure in the solid state,[15] and the structure of **5** can be regarded as a trimer of $PdCl_2$ cut out from the polymeric chain by two phosphane ligands. The formation of a $PdCl_2$ trimer terminated by organic ligands at each end has been postulated in some references, but based only on indirect evidence.[16] This is the first example of a structurally characterized $PdCl_2$ trimer complex. The bond length of Pd1−Cl3 is substantially longer than that of Pd1−Cl1, indicating the stronger *trans* influence of the phosphane ligand compared with that of the chloride. Similar asymmetry in the Pd−Cl bond lengths was reported for many dinuclear palladium chloride phosphane complexes, such as $[PdCl_2(PPh_3)_2]$.[17] On the other hand, there is no significant difference between the Pd2−Cl1 and Pd2−Cl3 bond lengths, both of which are close to the Pd−(μ-Cl) bond lengths in the central $PdCl_4$ unit of the chloride-bridged trinuclear Pd^{II} complex, $[Pd_3Cl_4(\mu^3\text{-}2\text{-methylallyl})_2]$ (2.30–2.31 Å).[18] It was found that **5** is solvated by ten molecules of $CHCl_3$ (omitted for clarity in Figure 4), all of which are located outside the cavity of the TRIP ligand.

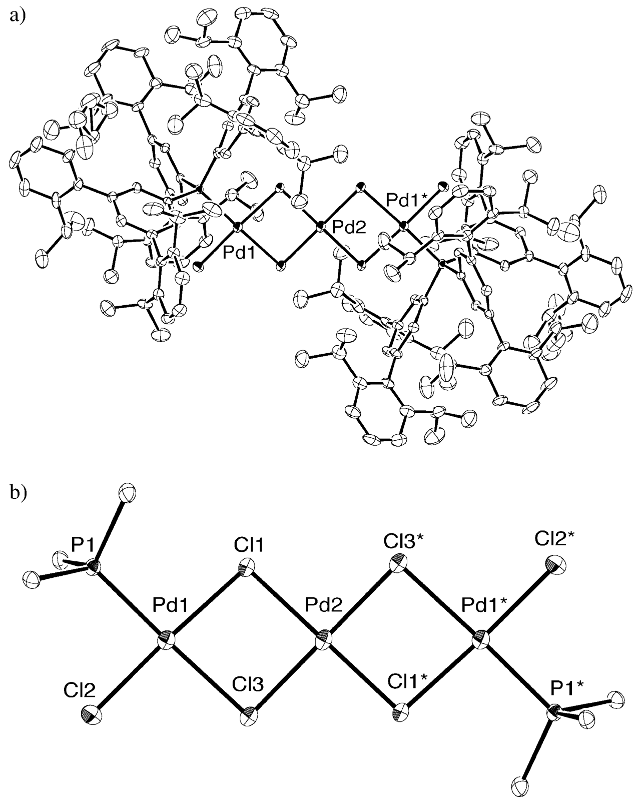


Figure 4. X-ray crystal structure of a) whole structure and b) partial structure of **5** (ORTEP drawing, 50% probability). Selected bond lengths [Å] and angles [°]: Pd1-Cl1, 2.3389(14); Pd1-Cl2, 2.2782(14); Pd1-Cl3, 2.4214(15); Pd1-P1, 2.2249(14); Pd2-Cl1, 2.2901(14); Pd2-Cl3, 2.3054(14); P1-Pd1-Cl3, 176.26(5); Cl1-Pd1-Cl2, 176.48(5).

It is noteworthy that the reaction of $PdCl_2$ with an excess of TRIP (three equivalents) also produced only trinuclear complex **5**; no dinuclear or mononuclear complexes were detected (Scheme 2). This is in sharp contrast with the reactions of tertiary phosphanes thus far reported, including TRMP, which produced $[PdCl_2(PR_3)_2]$-type complexes. The present results suggest that only one molecule of TRIP can coordinate to one palladium atom because the phosphorus center of TRIP is embedded in the bowl-shaped cavity, which is deeper than that of TRMP. On the other hand, the ^1H NMR spectrum of **5** in $CDCl_3$ at room temperature showed the signals for only one kind of isopropyl group; two non-equivalent methyl signals and one methyne signal were observed similar to *m*-terphenyl bromide **4**, thus indicating that there is a space around the phosphorus center large enough to ensure the rapid rotation of the P–C bonds. This space is largely due to the absence of any substituent in the ortho positions of phosphorus, which also contributes to the suppression of intramolecular metallation. Such an inert and large cavity in the ligand TRIP is considered to have enabled the formation of the $[(PdX_2)_3(PR_3)_2]$-type complex.

Experimental Section

Synthesis of TRIP: *tert*Butyllithium (2.36 M hexane solution, 6.14 mmol) was added to a solution of 5′-bromo-2,2″,6,6″-tetraisopropyl-1,1′:3′,1″-terphenyl (**4**)[6e] (1.42 g, 2.97 mmol) in THF (25 mL) at −70 °C under Ar. The mixture was stirred at −70 °C for 25 min. PCl_3 (84 µL, 0.963 mmol) was added to this solution and the mixture was stirred at −70 °C for 2.5 h and at room temperature for 2 h. After removal of the solvent, the residue was treated with degassed H_2O, and extracted with degassed $CHCl_3$ under Ar. The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was washed thoroughly with degassed ethanol to give TRIP as colorless crystals (0.475 g, 40%). M.p. 345 °C; ^1H NMR (500 MHz, $CDCl_3$) $\delta = 0.77$ (d, $J_{HH} = 6.8$ Hz, 36H), 0.95 (d, $J_{HH} = 6.8$ Hz, 36H), 2.52 (sept, $J_{HH} = 6.8$ Hz, 12H), 6.97 (s, 3H), 7.10 (d, $J_{HH} = 7.8$ Hz, 12H), 7.26 (t, $J_{HH} = 7.8$ Hz, 6H), 7.50 ppm (dd, $J_{PH} = 8.7$ Hz, $J_{HH} = 1.6$ Hz, 6H); ^{31}P NMR (109 MHz, $CDCl_3$) $\delta = -6.60$ ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) $\delta = 23.60$ (s), 23.99 (s), 30.38 (s), 122.41 (s), 127.91 (s), 131.58 (s), 133.45 (d, $J_{PC} = 23.2$ Hz), 135.60 (d, $J_{PC} = 13.7$ Hz), 138.77 (s), 140.61 (d, $J_{PC} = 8.6$ Hz), 146.61 ppm (s). Elemental analysis calcd (%) for $C_{90}H_{113}OP$: C 87.05, H 9.17; found: C 86.89, H 9.27. Atmospheric-pressure chemical ionization (APCI)-MS *m/z* 1224 $[M+H]^+$.

Synthesis of **5**: A solution of TRIP (134.9 mg, 0.110 mmol) in THF (30 mL) was added to a solution of $PdCl_2$ (29.8 mg, 0.168 mmol) in ethanol (10 mL). The mixture was heated at reflux for 3 h under Ar. After removal of the solvent, the residue was treated with $CHCl_3$ and filtered. After evaporation of the solvent, the residue was washed with hexane and recrystallized from $CHCl_3$/hexane to give **5** as yellow crystals (80.3 mg, 49%). M.p. 380 °C (decomp); ^1H NMR (500 MHz, $CDCl_3$) $\delta = 0.69$ (d, $J_{HH} = 6.8$ Hz, 72H), 0.89 (d, $J_{HH} = 6.8$ Hz, 72H), 2.53 (sept, $J_{HH} = 6.8$ Hz, 24H), 7.07 (d, $J_{HH} = 7.8$ Hz, 24H), 7.10 (s, 6H), 7.29 (t, $J_{HH} = 7.8$ Hz, 12H), 7.76 ppm (d, $J_{PH} = 9.3$ Hz, 12H); ^{31}P NMR (109 MHz, $CDCl_3$) $\delta = 34.77$ ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) $\delta = 23.64$ (s), 24.02 (s), 30.31(s), 122.65 (s), 126.72 (d, $J_{PC} = 57$ Hz), 128.10 (s), 133.72 (brs), 134.15 (s), 137.78 (s), 140.77 (m: virtual coupling), 146.80 ppm (s). Elemental analysis calcd (%) for $C_{180}H_{222}Cl_6P_2Pd_3$: C 72.56, H 7.51; found: C 72.27, H 7.79.

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Keywords: bowl-shaped molecules · palladium · phosphane ligands · steric hindrance · structure elucidation

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[1] For recent examples, see: a) S. Sasaki, K. Sutoh, F. Murakami, M. Yoshifuji, *J. Am. Chem. Soc.* **2002**, *124*, 14830; b) T. Hamada, A. Chieffi, J. Åhman, S. L. Buchwald, *J. Am. Chem. Soc.* **2002**, *124*, 1261; c) J. P. Stambuli, S. R. Stauffer, K. H. Shaughnessy, J. F. Hartwig, *J. Am. Chem. Soc.* **2001**, *123*, 2677; d) V. F. Slagt, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Angew. Chem.* **2001**, *113*, 4401; *Angew. Chem. Int. Ed.* **2001**, *40*, 4271; e) M. Naiki, S. Shirakawa, K. Kon-i, Y. Kondo, K. Maruoka, *Tetrahedron Lett.* **2001**, *42*, 5467; f) B. S. Balaji, Y. Obora, D. Ohara, S. Koide, Y. Tsuji, *Organometallics* **2001**, *20*, 5342.

[2] *Handbook of Organopalladium Chemistry for Organic Synthesis* (Ed.: E. Negishi), Wiley-Interscience, New York, **2002**.

[3] A. T. Hutton, C. P. Morley in *Comprehensive Coordination Chemistry, Vol. 5* (Ed.: G. Wilkinson), Pergamon, Oxford, **1987**, p. 1157.

[4] a) S. A. Dias, E. C. Alyea, *Transition Met. Chem.* **1979**, *4*, 205; b) E. C. Alyea, J. Malito, *J. Organomet. Chem.* **1988**, *340*, 119; c) E. C. Alyea, G. Ferguson, J. Malito, B. L. Ruhl, *Organometallics* **1989**, *8*, 1188.

[5] a) W. A. Herrmann, C. Brossmer, K. Öfele, C.-P. Reisinger, T. Priermeier, M. Beller, H. Fischer, *Angew. Chem.* **1995**, *107*, 1989; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1844; b) W. A. Herrmann, C. Brossmer, C.-P. Reisinger, T. H. Riermeier, K. Öfele, M. Beller, *Chem. Eur. J.* **1997**, *3*, 1357.

[6] For examples, see: a) K. Goto, N. Tokitoh, R. Okazaki, *Angew. Chem.* **1995**, *107*, 1202; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*,

1124; b) K. Goto, M. Holler, R. Okazaki, *J. Am. Chem. Soc.* **1997**, *119*, 1460; c) T. Saiki, K. Goto, R. Okazaki, *Angew. Chem.* **1997**, *109*, 2320; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2223; d) K. Goto, R. Okazaki, *Liebigs Ann./Recl.* **1997**, 2393; e) K. Goto, G. Yamamoto, B. Tan, R. Okazaki, *Tetrahedron Lett.* **2001**, *42*, 4875; f) K. Goto, Y. Hino, Y. Takahashi, T. Kawashima, G. Yamamoto, N. Takagi, S. Nagase, *Chem. Lett.* **2001**, 1204.

[7] a) K. Goto, Y. Hino, T. Kawashima, M. Kaminaga, E. Yano, G. Yamamoto, N. Takagi, S. Nagase, *Tetrahedron Lett.* **2000**, *41*, 8479; b) K. Goto, T. Okumura, T. Kawashima, *Chem. Lett.* **2001**, 1258; c) K. Goto, I. Shimo, T. Kawashima, *Bull. Chem. Soc. Jpn.*, in press.

[8] a) T. Kasai, T. Matsumoto, K. Tatsumi, *79th Spring Annual Meeting of the Chemical Society of Japan* (Tokyo, Japan) March 2001, Abstr. No. 1PA104; b) T. Matsumoto, T. Kasai, K. Tatsumi, *Chem. Lett.* **2002**, 346.

[9] a) K. Goto, Y. Ohzu, H. Sato, T. Kawashima, *15th International Conference on Phosphorus Chemistry* (Sendai, Japan), July 2001, Abstr. No. PB072; b) K. Goto, Y. Ohzu, H. Sato, T. Kawashima, *Phosphorus Sulfur Silicon Relat. Elem.* **2002**, *177*, 2179.

[10] TRMP and TRIP denote *tr*is(2,2″,6,6″-tetra*m*ethyl[1,1′:3′,1″-terphenyl]-5′-yl)*p*hosphane and *tr*is(2,2″,6,6″-tetra*i*sopropyl[1,1′:3′,1″-terphenyl]-5′-yl)*p*hosphane, respectively.

[11] O. Niyomura, M. Tokunaga, Y. Obora, T. Iwasawa, Y. Tsuji, *Angew. Chem.* **2003**, *115*, 1325; *Angew. Chem. Int. Ed.* **2003**, *42*, 1287.

[12] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313.

[13] Crystallographic data for TRIP·2CHCl$_3$: $C_{92}H_{113}Cl_6P$, $M_r = 1462.49$, triclinic, space group $P\bar{1}$, $a = 14.855(5)$, $b = 14.885(4)$, $c = 21.813(7)$ Å, $\alpha = 76.152(12)$, $\beta = 84.394(13)$, $\gamma = 67.948(10)°$, $V = 4340(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.119\ g\,cm^{-3}$, $T = 120$ K, $\mu(Mo_{K\alpha}) = 0.258\ mm^{-1}$, 28146 measured reflections, 14872 independent, 971 parameters, $R1 = 0.0816$ ($I > 2\sigma(I)$), $wR2 = 0.1865$ (all data). Crystallographic data for **5**·10CHCl$_3$: $C_{95}H_{116}Cl_{18}PPd_{1.5}$, $M_r = 2086.55$, triclinic, space group $P\bar{1}$, $a = 15.920(6)$, $b = 17.486(7)$, $c = 20.339(8)$ Å, $\alpha = 82.825(16)°$, $\beta = 71.934(14)°$, $\gamma = 74.785(14)°$, $V = 5189(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.336\ g\,cm^{-3}$, $T = 120$ K, $\mu(Mo_{K\alpha}) = 0.783\ mm^{-1}$, 33449 measured reflections, 17768 independent, 1075 parameters, $R1 = 0.0676$ ($I > 2\sigma(I)$), $wR2 = 0.1779$ (all data). The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated MoK$_\alpha$ radiation ($\lambda = 0.71069$ Å). The structures were solved by the direct method and refined by full-matrix least squares on F^2 using SHELXL 97 (G. M. Sheldrick, University of Göttingen, 1997). The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were idealized by using the riding models. CCDC-216987 (TRIP) and CCDC-216988 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[14] J. F. Blount, C. A. Maryanoff, K. Mislow, *Tetrahedron Lett.* **1975**, *16,* 913.

[15] P. M. Maitlis, P. Espinet, M. J. H. Russell in *Comprehensive Organometallic Chemistry, Vol. 6* (Ed.: G. Wilkinson), Pergamon, Oxford, **1982**, p. 233.

[16] a) R. Hüttel, H. J. Neugebauer, *Tetrahedron Lett.* **1964**, *5,* 3541; b) P. M. Maitlis, D. Pollock, M. L. Games, W. J. Pryde, *Can. J. Chem.* **1965**, *43*, 470; c) K. Tani, M. Yabuta, S. Nakamura, T. Yamagata, *J. Chem. Soc. Dalton Trans.* **1993**, 2781.

[17] J. Vicente, M. C. Lagunas, E. Bieuel, Cambridge Structural Database, refcode ROQZAY, **1997**.

[18] P. M. Bailey, E. A. Kelley, P. M. Maitlis, *J. Organomet. Chem.* **1978**, *144*, C52.