Synthesis, X-Ray Structure and Complexation Behavior of the New Tripodal Phosphane Ligand *cis,cis*-1,3,5-Tris[(diphenylphosphanyl)methyl]-1,3,5-trimethylcyclohexane (tdppmtmcy). Crystal Structure of Ir(tdppmtmcy)(CO)Cl

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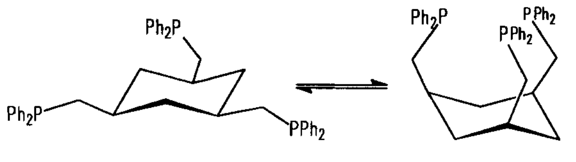
The introduction of three methyl groups into the *ipso* positions of the cyclohexane ring in *cis,cis*-1,3,5-tris[(diphenylphosphanyl)methyl]cyclohexane (tdppmcy) (**1**) leads to the new tripodal phosphane ligand *cis,cis*-1,3,5-tris[(diphenylphosphanyl)methyl]-1,3,5-trimethylcyclohexane (tdppmtmcy) (**5**). The dynamic behavior is studied by variable-temperature NMR spectroscopy and compared with the structure (X-ray analysis) in the solid state. Treatment of **5** with $Ir(PPh_3)_2(CO)Cl$ gives **6** where the two PPh_3 groups are replaced by two (diphenylphosphanyl)methyl groups of the ligand **5**. In addition, an intramolecular C—H metalation takes place resulting in the oxidative addition of a ring methylene C—H bond to the metal. The X-ray structure of **6** is determined.

Transition metal complexes coordinated to polyphosphane ligands are attracting considerable interest because of their potential use as homogeneous catalysts[2]. Tripodal ligands are especially interesting because they characteristically form complexes with different coordination geometries[3]. We have recently reported on the synthesis and complexation chemistry of the new tripodal ligand **1**[4].

Scheme 1



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Since the three (diphenylphosphanyl)methyl groups are specifically bound in the *cis,cis*-1,3,5-position to the cyclohexane ring, the coordination geometry imposed by **1** on a metal center is a function of the bite angle of the phosphane donors as well as of the conformation and the flexibility of the cyclohexane ring. Thus, no facial geometry is adopted when **1** is coordinated to a trigonal-bipyramidal or an octahedral metal center in spite of the C_{3v} symmetry of **1**[5]. In order to study the significance of metal-coordinated (diphenylphosphanyl)methyl groups in the axial or equatorial position, we have introduced bulky substituents into the *ipso* positions of **1**.

Results and Discussion

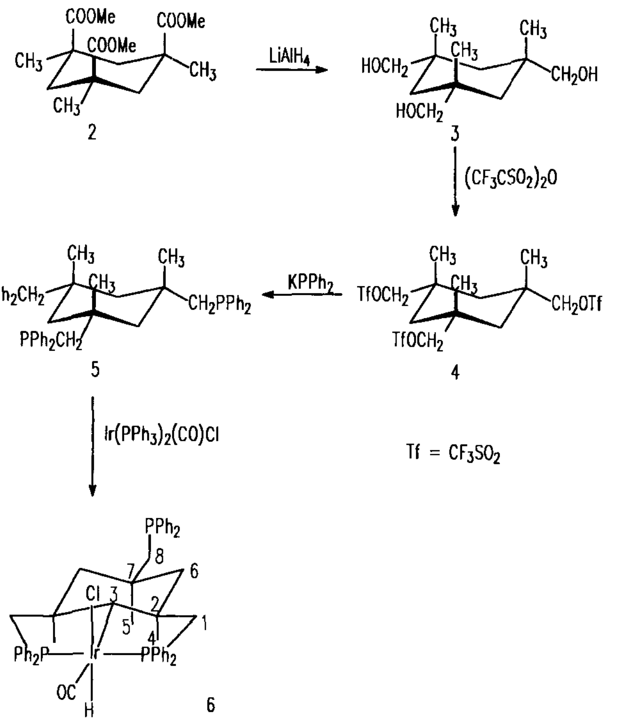
Ligand Synthesis

The interaction between two or more diaxial substituents on the same side of a cyclohexane ring has been found to be of rather high energy[6]. The ground-state structure of the trimethyl ester **2** (Scheme 2) prefers the methyl groups in the equatorial and the ester groups in the axial orientations. This has been shown by NMR spectroscopy[7] and by a single-crystal X-ray analysis[8]. Consequently, we have chosen **2** as the starting material for the synthesis of *cis,cis*-1,3,5-tris[(diphenylphosphanyl)methyl]-1,3,5-trimethylcyclohexane (tdppmtmcy) (**5**), which has been prepared in three steps (Scheme 2). The reduction of **2** with an excess of $LiAlH_4$ in THF results in the triol **3**, which is soluble in THF and dioxane. Treatment of **3** with a stoichiometric amount of trifluoromethanesulfonic anhydride in the presence of pyridine gives the triflate **4**, which is isolated as a colorless solid that decomposes at room temperature within days but is stable for a longer period of time when stored below −10 °C. Treatment of **4** with an equimolar amount of $KPPh_2$ in THF results in **5** as a colorless solid.

The ^1H- and ^{13}C-NMR spectra of **3**–**5** are consistent with a C_{3v} symmetry of the compounds and thus confirm the *cis,cis* arrangement of the functional groups on the cyclohexane ring. Hence, the alkane region of the $^{13}C\{^1H\}$-NMR spectra of **3**–**5** shows four signals: those of the methyl, the ring methylene, and the α-methylene groups, as well as the quaternary carbon atoms. In the case of **5** each signal is split by the interaction with the phosphorus nuclei. The strong downfield shift ($\delta = 86.7$) of the α-methylene group signals of **4** reflects the high electron-withdrawing ability of the triflate function and its property as an efficient leaving group. The ^1H-NMR spectra of **3**–**5** display singlets due to the methyl groups and the α-methylene protons in the case of the triflate, while the α-methylene protons of **3** and **5** show doublets caused by the coupling of the hydroxy protons and the phosphorus nuclei, respectively.

Characteristic and conformation-sensitive features in the ^1H-NMR spectra of **3**–**5** are the AB patterns observed for

Scheme 2



the equatorial (H_e) and axial (H_a) protons of the ring methylene groups. The 1,3,5-positions of the geminal functional groups cause a repulsion between the *syn*-axial substituents which, depending on the size of the substituents, leads to a flattening of the ring[9]. Due to this deformation the chair conformations of **3**–**5** are able to invert fast because the ground-state structure has approached the transition-state geometry of the ring inversion[9b]. This is demonstrated by the small chemical shift difference at room temperature of the ring methylene hydrogen atoms of $\Delta\delta = 0.19$, 0.20, and 0.21, respectively, in the cases of **3**–**5** compared to $\Delta\delta = 1.51$ and 1.71 for **1** and **2**. This indicates that the effect of the diamagnetic anisotropy of the carbon-carbon bond[10] on the chemical shift of the ring methylene hydrogen atoms is averaged by the fast ring inversion. The intrinsic differences of the chemical shifts due to the different orientations of the ring methylene hydrogen atoms with respect to the neighboring functional groups (here: CH_3 vs. CH_2OH, CH_2OTf, CH_2PPh_2), however, remain. Thus, the AB patterns of **3** and **4** show a small temperature-dependent chemical shift and are basically invariant. A different behavior of the ring methylene protons is observed when a sample of **5** is heated to 100°C. In [D$_5$]pyridine the high-field part of the AB spectrum is shifted to lower field while the low-field part remains constant. When [D$_8$]toluene is used as the solvent both resonances are shifted towards one another pretending a coalescence at 75°C.

The X-ray crystal structures of **3** and **5** (Figures 1 and 2) establish the *cis,cis* arrangement of the functional groups. In contrast to **2**[8], the methyl groups are oriented triaxially in the crystal. In both cases the cyclohexane ring prefers the chair conformation as the ground-state structure. The chairs are flattened, which is reflected by the widening of the endocyclic bond angles of the ring carbon atoms between those to which the functional groups are attached to 117.4° (**3**) and up to 119.9° (**5**) and the decrease of the ring torsional angles to +/−48.5° (**3**) and +/−47.3° (average value) (**5**) compared to 111.5° and +/−55° in cyclohexane[11]. This is in close agreement with 1,1,3,3,5,5-hexamethylcyclohexane where the torsional and the endocyclic bond angles have been calculated to be +/−47° and 118°, respectively[9b]. In this case the ring inversion is too fast to be detected by NMR spectroscopy in solution.

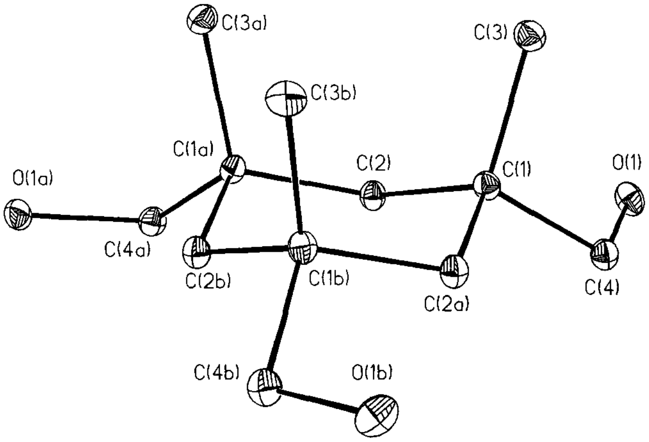


Figure 1. ORTEP plot of the alcohol **3**; thermal ellipsoids are drawn at the 30% level; symmetry transformations: $a = 1 - y, 1 + x - y, z$; $b = y - x, 1 - y, z$; selected bond distances [pm]: C(1)–C(2) 153.9(2), C(1)–C(3) 154.5(3), C(1)–C(4) 153.7(3), C(4)–O(1) 142.2(2); bond angles [°]: C(3)–C(1)–C(4) 107.1(2), C(2)–C(1)–C(2A) 109.6(2), C(3)–C(1)–C(2A) 112.3(1), C(1)–C(2)–(C1A) 117.4(2), C(1)–C(4)–O(1) 113.2(1); torsional angles [°]: C(3)–C(1)–C(2)–C(1A) −78.0(0.2), C(4)–C(1)–C(2)–C(1A) 163.6(0.1), C(2A)–C(1)–C(2)–C(1A) 48.5(0.3)

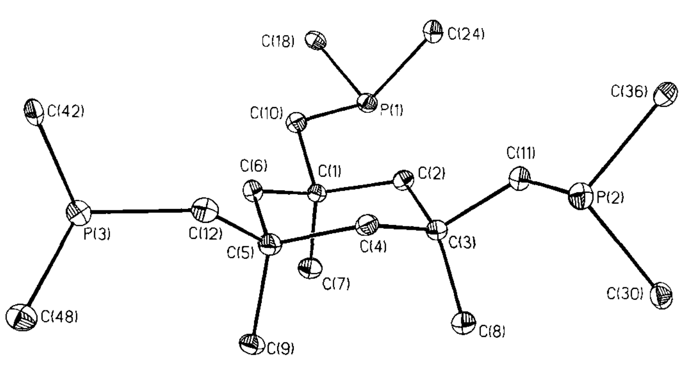


Figure 2. ORTEP plot of the tdppmtmcy ligand **5**; thermal ellipsoids are drawn at the 30% level; only the *ipso* carbon atoms of the phenyl rings are shown for clarity; selected bond distances [pm]: P(1)–C(10) 185.7(4), P(1)–C(18) 185.5(3), C(1)–C(10) 156.0(6), C(1)–C(2) 152.9(5), C(1)–C(7) 152.5(5); bond angles [°]: C(1)–C(2)–C(3) 119.9(3), C(2)–C(3)–C(4) 108.3(3), C(3)–C(4)–C(5) 118.7(3), C(4)–C(5)–C(6) 108.5(3), C(1)–C(6)–C(5) 118.8(3); torsional angles [°]: C(1)–C(2)–C(3)–C(4) −46.6(0.4), C(2)–C(1)–C(6)–C(5) −46.6(0.4), C(3)–C(4)–C(5)–C(6) −48.7(0.4)

Complexation

Treatment of tdppmtmcy with Ir(PPh$_3$)$_2$(CO)Cl in hot toluene gives the octahedral complex **6** (Scheme 2) as a pale yellow powder. In spite of the high flexibility of the cyclohexane ring of the ligand, only two (diphenylphosphanyl)methyl groups have been found to coordinate to the metal center. Thus, the $^{31}P\{^1H\}$-NMR spectrum shows a singlet of intensity 2 at $\delta = 32.1$ due to the phosphorus bound to the metal and a singlet of intensity 1 at $\delta = -26.4$ caused by the noncoordinated (diphenylphosphanyl)methyl group. The ^1H-NMR spectrum of **6** displays the hydride resonance signal as a triplet at $\delta = -17.70$. The magnitude of the phosphorus-hydrogen coupling constant ($^2J_{PH} = 10.61$ Hz) is typical of a hydrogen atom *cis* to a phosphorus atom[12]. A singlet is observed at $\delta = 2.62$ for the hydrogen atom bound to the metalated carbon atom. Both diastereotopic protons of the methylene groups in the five-membered rings give rise to A parts of AMXX′ (M = H, XX′ = PP′) multiplets ($\delta = 2.42$, $N = 8.33$ Hz; $\delta = 2.82$, $N = 8.33$ Hz), which is indicative of two phosphorus atoms being coordinated *trans*[13]. All other proton resonances of the ligand are in agreement with a mirror plane symmetry of the complex. This is also confirmed by the $^{13}C\{^1H\}$-NMR spectrum. The AXX′ (XX′ = PP′) patterns for the α-methylene carbon atoms (C-1) and the quaternary carbon atoms (C-2) of the five-membered rings at $\delta = 49.27$ ($N = 32.20$ Hz) and 47.24 ($N = 14.80$ Hz) are consistent with two phosphorus atoms in *trans* position. The signals of the methyl group C-4 and the carbon atom attached to the iridium atom (C-3) are observed as singlets at $\delta = 26.69$ and 68.67, respectively. While the signals of the remaining carbon atoms at $\delta = 30.05$ (C-5), 36.65 (C-7), 51.78 (C-8) are only coupled to the noncoordinated phosphorus nucleus, the signal of C-6 at $\delta = 52.63$ shows an interaction with both phosphorus sites. The observation of long-range couplings (four bonds) in the ^1H- and $^{13}C\{^1H\}$-NMR spectra is characteristic of a rigid system. This is due to the condensation of two five-membered heterocycles with the cyclohexane ring which is caused by the intramolecular oxidative addition of a ring C–H bond to a Vaska-type complex. Compound **6** represents a rare example of a cyclometalation involving CH_2 groups from cyclohexane rings[4,14].

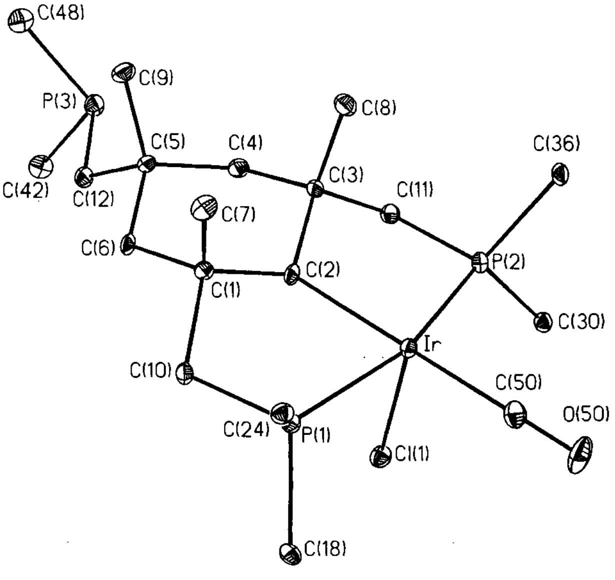


Figure 3. ORTEP plot of the iridium complex **6**; thermal ellipsoids are drawn at the 30% level; only the *ipso* carbon atoms of the phenyl rings are shown for clarity; selected bond distances [pm]: Ir–Cl(1) 249.5(2), Ir–C(50) 190.6(6), Ir–P(1) 230.4(1), Ir–P(2) 230.5(1), Ir–C(2) 216.5(5), C(50)–O(50) 112.9(8); bond angles [°]: P(1)–Ir–P(2) 163.5(1), C(50)–Ir–P(1) 97.4(2), C(50)–Ir–P(2) 99.0(2), C(50)–Ir–C(2) 177.8(3)

An ORTEP drawing of the single-crystal X-ray structure analysis of **6** which confirms the molecular constitution established by NMR spectroscopy is shown in Figure 3. The geometry around Ir is best described as distorted octahedral. The chloride and the hydride (could not be located from a difference map) occupy the apical positions. The two mutual *trans* phosphorus atoms and the carbon atom C-2 of the tdppmtmcy ligand and the carbon monoxide form the equatorial plane. The deviation of the P1–Ir–P2 angle [163.5(1)°] from linearity opens the C50–Ir–P1 and C50–Ir–P2 angles to 97.4(2) and 99.0(2)°, respectively. In a further structural detail it is clearly demonstrated that the equatorial C–H bond is metalated.

The ν(IrH) band at $\tilde{\nu} = 2194$ cm^{-1} in the infrared spectrum is characteristic of hydrogen atoms *trans* to chloride[15a], and the ν(CO) band at $\tilde{\nu} = 1992$ cm^{-1} is in agreement with octahedral Ir(III) complexes[15].

Conclusion

The introduction of three methyl groups into the *ipso* position of the cyclohexane ring in **1** leads to the new tripodal ligand **5**. The sp^2 carbon atoms of the carboxyl groups in **2** are sterically less demanding than the sp^3 carbon atoms of the α-methylene groups in **3**–**5**. This causes a higher 1,3-interaction and thus a flattening of the cyclohexane ring, which has been shown by single-crystal X-ray investigations for **3** and **5**. Therefore, in contrast to **2**, the tdppmtmcy ligand is much more flexible in solution. In spite of this flexibility only two phosphane groups are coordinated to the metal center in **6**. The strong 1,3-interaction of the three methyl groups obviously prevents the coordination of all three phoshane sites to iridium.

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Experimental

All manipulations were performed under pure argon by using standard Schlenk techniques. All solvents were carefully dried and stored under argon. THF was freshly distilled from sodium/benzophenone prior to use. Trimethyl *cis,cis*-1,3,5-trimethyl-1,3,5-trimethylcyclohexanetricarboxylate[16] (**2**) and $Ir(PPh_3)_2(CO)Cl$[17] were prepared according to literature procedures.

MS (FD, EI): Finnigan MAT 711 A modified by AMD (8 kV, 60°C). – IR: Bruker IFS 48. – $^{31}P\{^1H\}$ NMR: Bruker WP 80 and AC 80 (32.39 and 32.44 MHz; ext. standard 1% H_3PO_4/[D_6]acetone. – ^1H and $^{13}C\{^1H\}$NMR: Bruker AC 250 (250.13 and 62.90 MHz; int. standard TMS). In addition to the $^{13}C\{^1H\}$-NMR spectrum a ^{13}C-DEPT[18] experiment was routinely recorded for each compound. – Single-crystal X-ray structure determination of

3, **5**, and **6**: Siemens P4 diffractometer. – Elemental analysis: Carlo Erba 1106.

cis,cis-1,3,5-Tris(hydroxymethyl)-1,3,5-trimethylcyclohexane (**3**): A solution of 20.0 g (67.0 mmol) of trimethyl *cis,cis*-1,3,5-trimethylcyclohexanetricarboxylate (**2**) in 75 ml of THF was added dropwise to an ice-cooled suspension of 10.0 g (26.4 mmol) of $LiAlH_4$ in 300 ml of THF. After refluxing of the reaction mixture for 16 h and cooling to 0°C, the salts were decomposed with water/ethanol (1:4) (ca. 200 ml). The suspension was refluxed for 4 h, the resulting precipitate was filtered hot, and the solids were washed with hot ethanol (3 × 150 ml). The solvent was removed under reduced pressure, and the solid residue was extracted in a Soxhlet apparatus with 1,3-dioxane (500 ml). Evaporation of the 1,3-dioxane in vacuo and recrystallization of the colorless powder from THF yielded 8.6 g (60%) of **3**; m.p. 176°C. – ^1H NMR ($[D_6]DMSO$): $\delta = 0.93$ (d, $^2J_{HH} = 13.9$ Hz, 3H, CH_aH_e), 1.00 (s, 9H, CH_3), 1.13 (d, $^2J_{HH} = 13.9$ *Hz, 3H*, CH_aH_e), 2.93 (d, $^3J_{HH} = 5.38$ Hz, 6H, CH_2OH), 4.47 (t, $^3J_{HH} = 5.38$ Hz, CH_2OH). – $^{13}C\{^1H\}$NMR ($[D_6]DMSO$): $\delta = 25.95$ (s, CH_3), 35.11 [s, $(CH_2)_2CCH_3$], 40.20 (s, CCH_2C), 74.10 (s, CH_2OH). – MS (FAB): $m/z = 217$ $[C_{12}H_{24}O_3^+]$. – $C_{12}H_{24}O_3$ (216.3): calcd. C 66.63, H 11.18; found C 66.81, H 11.32.

X-Ray Structure Determination of **3**[19]: Single crystals with the dimensions 0.25 × 0.25 × 0.40 mm were grown from THF. Siemens P4 diffractometer; graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å); formula $C_{12}H_{24}O_3$; mol. mass 216.3; space group $R3$ (No. 146); lattice constants: $a = 1305.3(7)$, $c = 614.6(4)$ pm; $V = 907.1(9) \cdot 10^6$ pm³; $\varrho_{calcd.} = 1.188$ g/cm³; $Z = 3$; μ(Mo-K_α) = 0.083 mm^{-1}; $2\Theta = 4-50°$; ω scan; scan speed variable (3 to 30°/min in ω); scan range 1.2°; *hkl*: −15→15, −15→15, −7→7; 2130 reflections measured, 712 unique and 647 considered observed [$I > 2\sigma(I)$]; 77 variables. The structure was solved by direct methods[20]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located from a difference map and included in the final refinement with individual U_i. $R = 0.026$; $R_w = 0.028$, $S = 0.81$. Maximum and minimum peaks in the final difference synthesis were 0.26 and −0.25 eÅ^{-3}, respectively. Final atomic coordinates are given in Table 1.

Table 1. Atomic coordinates ($\cdot 10^4$) and equivalent isotropic thermal parameters ($\cdot 10^3$ Å^2) for the alcohol **3**

Atom	x	y	z	U_{eq}
C(1)	2659(1)	7336(1)	4044(3)	19(1)
C(2)	2049(1)	6022(1)	3395(3)	20(1)
C(3)	2487(1)	7538(2)	6462(3)	25(1)
C(4)	2101(1)	7918(2)	2680(3)	22(1)
O(1)	856(1)	7379(1)	2965	26(1)

cis,cis-1,3,5-Trimethyl-1,3,5-tris[(trifluoromethylsulfonyloxy)methyl]cyclohexane (**4**): A suspension of 0.80 g (3.70 mmol) of **3** and 0.9 ml of pyridine in 20 ml of CH_2Cl_2 was slowly added to an ice-cooled solution of 1.80 ml (11.1 mmol) of trifluoromethanesulfonic anhydride (freshly distilled) in 15 ml of CH_2Cl_2. After stirring the mixture for 2 h at 0°C, the precipitate was filtered, and the solution passed through a column of silica gel. Removal of the solvent under reduced pressure afforded 1.85 g (82%) of **4** as an off-white powder which decomposes within days at room temp. Spectroscopic data have been obtained at room temp.; m.p. 76°C (dec.). – ^1H NMR ($CDCl_3$): $\delta = 1.24$ (d, $^2J_{HH} = 14.1$ Hz, 3H, CH_aH_e), 1.32 (s, 9H, CH_3), 1.44 (d, $^2J_{HH} = 14.1$ Hz, 3H, CH_aH_e), 4.06 (s, 6H, CH_2OTf). – $^{13}C\{^1H\}$NMR ($CDCl_3$): $\delta = 24.05$ (s, CH_3), 34.77 [s, $(CH_2)_2CCH_3$], 37.85 (s, CCH_2C), 86.73 (s, CH_2OTf), 118.40 (q, $^1J_{FC} = 319.38$ Hz, CF_3). – No interpretable mass spectrum could be obtained. – $C_{15}H_{21}F_6O_9S_3$ (612.5): calcd. C 29.41, H 3.46, F 27.92, S 15.70; found C 29.30, H 3.33, F 27.27, S 16.05.

cis,cis-1,3,5-Tris[(diphenylphosphanyl]methyl]-1,3,5-trimethylcyclohexane (**5**): To a suspension of 0.44 g (11.0 mmol) of KH in 30 ml of THF was added dropwise a solution of 1.60 g (8.60 mmol) of $HPPh_2$ in 10 ml of THF. After stirring for 3 h, the red solution was filtered and a solution of 1.72 g (2.80 mmol) of **4** in 15 ml of THF was added dropwise. The reaction mixture was stirred for an additional 16 h, hydrolyzed, and the organic layer separated and dried with silica gel. Removal of the solvent and recrystallization of the residue from CH_2Cl_2 gave 1.40 g (69%) colorless crystals; m.p. 145°C. – ^1H NMR (CD_2Cl_2): $\delta = 1.17$ (s, 9H, CH_3), 1.45 (d, $^2J_{HH} = 13.82$ Hz, 3H, CH_aH_e), 1.66 (d, $^2J_{HH} = 13.82$ Hz, 3H, CH_aH_e), 2.08 (d, $^2J_{PH} = 4.06$ Hz, 6H, CH_2P), 7.25–7.32 (m, 12H, *o*-C_6H_5), 7.33–7.42 (m, 18H, *m,p*-C_6H_5). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 29.3$

Table 2. Atomic coordinates ($\cdot 10^4$) and equivalent isotropic thermal parameters ($\cdot 10^3$ Å^2) for the tdppmtmcy ligand **5**

Atom	x	y	z	U_{eq}
P(1)	2480(1)	3998(1)	1897(1)	30(1)
P(2)	3943(1)	-451(1)	1721(1)	33(1)
P(3)	2080(1)	1292(1)	3945(1)	31(1)
C(1)	1682(4)	2510(3)	2439(1)	26(1)
C(2)	2369(4)	1980(2)	2059(1)	27(1)
C(3)	2225(4)	991(3)	2056(1)	27(1)
C(4)	2519(4)	656(2)	2545(1)	29(1)
C(5)	1798(4)	1103(3)	2956(1)	29(1)
C(6)	1990(4)	2084(2)	2907(1)	28(1)
C(7)	136(4)	2660(3)	2356(1)	36(1)
C(8)	838(4)	669(3)	1863(2)	38(1)
C(9)	272(4)	835(3)	3003(1)	32(1)
C(10)	2384(4)	3416(3)	2453(1)	32(1)
C(11)	3397(4)	687(3)	1731(1)	33(1)
C(12)	2570(4)	792(2)	3389(1)	31(1)
C(13)	3009(3)	5394(2)	2532(1)	32(1)
C(14)	3343	6251	2625	37(2)
C(15)	3688	6809	2267	43(2)
C(16)	3698	6509	1815	41(2)
C(17)	3364	5651	1722	36(1)
C(18)	3019	5094	2080	31(1)
C(19)	5398(3)	3691(2)	1905(1)	36(1)
C(20)	6629	3367	1720	45(2)
C(21)	6621	2972	1290	49(2)
C(22)	5382	2901	1044	49(2)
C(23)	4151	3225	1229	41(2)
C(24)	4159	3620	1659	31(1)
C(25)	2018(3)	-1671(2)	1456(1)	39(1)
C(26)	1132	-2106	1156	46(2)
C(27)	998	-1830	702	44(2)
C(28)	1751	-1117	549	42(2)
C(29)	2637	-681	849	39(1)
C(30)	2770	-958	1302	31(1)
C(31)	6315(3)	-1108(1)	1324(1)	41(2)
C(32)	7602	-1094	1105	46(2)
C(33)	8126	-319	933	47(2)
C(34)	7362	440	980	42(2)
C(35)	6075	425	1200	36(1)
C(36)	5551	-349	1372	33(1)
C(37)	4327(3)	337(1)	4324(1)	37(2)
C(38)	5634	268	4527	55(2)
C(39)	6360	1011	4652	59(2)
C(40)	5778	1822	4574	59(2)
C(41)	4471	1890	4371	43(2)
C(42)	3745	1148	4246	32(1)
C(43)	627(3)	737(2)	4698(1)	40(2)
C(44)	-202	193	4964	54(2)
C(45)	-653	-594	4786	59(2)
C(46)	-276	-838	4342	57(2)
C(47)	553	-294	4076	44(2)
C(48)	1004	492	4254	36(1)
Cl(1)	3042(2)	2452(1)	-37(1)	90(1)
Cl(2)	1132(3)	1488(2)	532(1)	133(1)
C(50)	2257(9)	1465(4)	78(3)	103(3)

(d, $^3J_{PC}$ = 10.78 Hz, CH_3), 36.1 [d, $^2J_{PC}$ = 13.32 Hz, $(CH_2)_2CCH_3$], 49.8 (d, $^1J_{PC}$ = 6.48 Hz, CH_2P), 51.1 (t, $^3J_{PC}$ = 10.25 Hz, CCH_2C), 128.5 (s, *p*-C_6H_5), 128.65 (d, $^3J_{PC}$ = 6.80 Hz, *m*-C_6H_5), 133.2 (d, $^2J_{PC}$ = 19.82 Hz, *o*-C_6H_5), 140.9 (d, $^1J_{PC}$ = 13.19 Hz, *i*-C_6H_5). – $^{31}P\{^1H\}$ NMR (THF, −30°C): $\delta = -27.1$ (s). – MS (FAB): *m/z* = 720 [$C_{48}H_{51}P_3^+$]. – $C_{48}H_{51}P_3 \cdot CH_2Cl_2$ (805.8): calcd. C 73.04, H 6.63, Cl 8.80; found C 73.40, H 6.58, Cl 8.49.

X-Ray Structure Determination of **5**[19]: Single crystal dimensions 0.5 × 0.5 × 0.5 mm. Siemens P4 diffractometer, graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å); formula $C_{48}H_{51}P_3 \cdot CH_2Cl_2$; mol. mass 805.7; space group $P2_12_12_1$ (No. 19); lattice constants: a = 962.7(2), b = 1550.5(3), c = 2912.2(6) pm; V = 4347.2(2) · 10^6 pm^3; $\varrho_{calcd.}$ = 1.231 g/cm^3; Z = 4; μ(Mo-K_α) = 0.293 mm^{-1}; 2Θ = 4–40°; ω scan; scan speed variable (10 to 30°/min in ω); scan range = 1.4°; *hkl*: $-9 \rightarrow 9$, $-14 \rightarrow 14$, $-28 \rightarrow 28$; 16175 reflections measured, 4056 unique and 3791 considered observed [$I > 2\sigma(I)$]; 415 variables. The structure was solved by direct methods[20]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were in calculated positions (riding model) and the phenyl substituents were treated as rigid groups. R = 0.036, R_w = 0.038, S = 1.07. Maximum and minimum peaks in the final difference synthesis were 0.66 and −0.45 eÅ^{-3}, respectively. The crystal contains one solvent molecule of CH_2Cl_2. Final atomic coordinates are given in Table 2.

Table 3. Atomic coordinates (· 10^4) and equivalent isotropic thermal parameters (· 10^3 Å^2) for thc iridium complex **6**

Atom	x	y	z	U_{eq}
Ir	1692(1)	3844(1)	6910(1)	17(1)
Cl(1)	3207(1)	4838(1)	7132( )	26(1)
C(50)	1495(5)	4591(5)	5804(4)	28(2)
O(50)	0.1322(5)	5036(5)	5161(3)	47(2)
P(1)	373(1)	5058(1)	7694(1)	19(1)
P(2)	3124(1)	2412(1)	6511(1)	19(1)
P(3)	3478(2)	365(1)	10962(1)	29(1)
C(1)	819(5)	3263(4)	8870(4)	18(2)
C(2)	1846(5)	2989(5)	8173(3)	19(2)
C(3)	2398(5)	1768(4)	8198(4)	19(2)
C(4)	2786(5)	1406(5)	9096(4)	24(2)
C(5)	1877(5)	1670(5)	9884(4)	23(2)
C(6)	1219(5)	2867(5)	9756(3)	20(2)
C(7)	-280(5)	2858(5)	8780(4)	28(2)
C(8)	1712(6)	970(5)	7958(4)	27(2)
C(9)	1068(6)	822(5)	10128(4)	29(2)
C(10)	521(5)	4536(5)	8808(4)	21(2)
C(11)	3497(5)	1723(5)	7539(4)	22(2)
C(12)	2499(6)	1652(5)	10668(4)	26(2)
C(13)	570(4)	6999(3)	6685(2)	36(2)
C(14)	878	8031	6465	37(2)
C(15)	1258	8534	7069	39(2)
C(16)	1328	8004	7893	34(2)
C(17)	1020	6971	8112	27(2)
C(18)	640	6469	7508	20(2)
C(19)	-1467(3)	4917(3)	6872(2)	24(2)
C(20)	-2620	5114	6774	25(2)
C(21)	-3431	5664	7372	30(2)
C(22)	-3089	6016	8069	35(2)
C(23)	-1937	5819	8168	30(2)
C(24)	-1126	5269	7569	21(2)
C(25)	4302(3)	3295(4)	5041(2)	36(2)
C(26)	5242	3631	4515	37(2)
C(27)	6295	3452	4812	31(2)
C(28)	6409	2937	5635	33(2)
C(29)	5470	2602	6160	28(2)
C(30)	4417	2781	5863	22(2)
C(31)	1870(3)	1655(3)	5437(3)	40(3)
C(32)	1696	921	4904	52(3)
C(33)	2466	-62	4810	39(3)
C(34)	3409	-311	5250	39(3)
C(35)	3583	423	5784	31(2)
C(36)	2813	1406	5877	22(2)
C(37)	5206(4)	1390(4)	11199(2)	39(3)
C(38)	5851	1886	11634	50(3)
C(39)	5566	1939	12514	49(3)
C(40)	4637	1496	12959	46(3)
C(41)	3993	1000	12524	38(2)
C(42)	4277	947	11644	33(2)
C(43)	2981(4)	-1581(3)	11779(3)	43(3)
C(44)	2406	-2298	12356	56(4)
C(45)	1455	-1883	12919	51(3)
C(46)	1080	-750	12904	47(3)
C(47)	1655	-32	12327	38(2)
C(48)	2606	-448	11765	34(2)
C(49)	4060(8)	5088(8)	9073(5)	53(3)
Cl(2)	4574(3)	3710(2)	9409(2)	75(1)
Cl(3)	2908(2)	5635(2)	9806(2)	62(1)

(OC-6-53)-Carbonylchlorohydrido{cis,cis-2,4,6-tris[(diphenylphosphanyl-κ^{2}P$_1$P$_2$)methyl]-2,4,6-trimethylcyclohexyl-κC$_1$}iridium(III) (**6**): 108 mg (0.15 mmol) of **5** and 117 mg (0.15 mmol) of $Ir(PPh_3)_2(CO)Cl$ were heated in 30 ml of toluene under reflux for 3 h. The solution was concentrated to 15 ml, and 30 ml of *n*-hexane was added. The pale yellow precipitate was filtered and washed with pentane to yield 107 mg (73%) of **6**; m.p. 197°C (dec.). – ^1H NMR (CD_2Cl_2): $\delta = -17.70$ (t, $^2J_{PH}$ = 10.61 Hz, 1H, IrH), 0.73 (s, 6H, CH_3), 1.22 (s, 3H, CH_3), 1.42 (d, $^2J_{HH}$ = 13.76 Hz, 2H, CH_aH_e), 2.16 (d, $^2J_{PH}$ = 4.46 Hz, 2H, CH_2P), 2.22 (d, $^2J_{HH}$ = 13.76 Hz, 2H, CH_aH_e), 2.42 (m, $^2J_{HH}$ = 12.94 Hz, N = 8.33 Hz, 2H, PCH_aH_e), 2.62 (s, 1H, IrCH), 2.82 (m, $^2J_{HH}$ = 12.94 Hz, N = 8.33 Hz, 2H, PCH_aH_e), 7.10–7.95 (m, 30H, C_6H_5). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 26.69 (s, $IrPCH_2CCH_3$), 30.05 (d, $^3J_{PC}$ = 11.67 Hz, PCH_2CCH_3), 36.65 (d, $^2J_{PC}$ = 12.63 Hz, PCH_2C), 47.24 (m, N = 14.80 Hz, $IrPCH_2C$), 49.27 (m, N = 32.20 Hz, $IrPCH_2$), 51.78 (d, $^1J_{PC}$ = 16.5 Hz, PCH_2), 52.63 (dt, $^3J_{PC}$ = 9.5 Hz, CH_2 ring), 68.67 (s, IrCH), 128.0–142.4 (m, C_6H_5), 176.0 (t, $^2J_{PC}$ = 7.1 Hz, IrCO). – $^{31}P\{^1H\}$ NMR (CH_2Cl_2, −30°C): $\delta = -26.4$ (s, 1 P, PCH_2), 32.1 (s, 2 P, IrP). – No interpretable mass spectrum could be obtained. – $C_{49}H_{51}ClIrOP_3 \cdot CH_2Cl_2$ (1061.5): calcd. C 56.58, H 5.03, Cl 10.02; found C 56.21, H 5.13, Cl 9.5.

X-Ray Structure Determination of **6**[19]: Single crystal with dimensions 0.1 × 0.1 × 0.2 mm. Siemens P4 diffractometer; graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å); formula: $C_{49}H_{51}ClIrOP_3 \cdot CH_2Cl_2$; mol. mass 1061.4; space group $P\bar{1}$ (No. 2); lattice constants: a = 1207.1(2), b = 1247.4(2), c = 1592.9(3) pm; α = 82.29(3), β = 80.67(3)°, γ = 78.67(3)°; V = 2307.6(7) · 10^6 pm^3; $\varrho_{calcd.}$ = 1.528 g/cm^3; Z = 2; μ(Mo-K_α) = 3.207 mm^{-1}; 2Θ = 4–50°; Wyckoff scan; scan speed: variable (5 to 30°/min); scan range = 1.2°; *hkl*: $-14 \rightarrow 11$, $-14 \rightarrow 14$, $-18 \rightarrow 18$; 15643 reflections measured, 8137 unique and 6669 considered observed [$I > 2\sigma(I)$]; 451 variables. An absorption correction was applied (Ψ scan, maximum and minimum transmission 0.55 and 0.42, respectively). The structure was solved by Patterson synthesis[20]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were in calculated positions (riding model), and the phenyl substituents were treated as rigid groups. R = 0.039, R_w = 0.038, S = 0.72. Maximum and minimum peaks in the final difference synthesis were 1.21 and −1.56 eÅ^{-3}, respectively. The crystal contains one solvent molecule of CH_2Cl_2. Final atomic coordinates are given in Table 3.

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[1] X-ray structure determination.

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