cis,cis-1,3,5-Tris(diphenylphosphino)cyclohexane (tdppcy). A new tripodal phosphine that forms metal complexes with adamantane-type structures. Crystal structure of Ir(tdppcy)Cl$_3$ *

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Abstract

The novel tridentate phosphine *cis,cis*-1,3,5-tris(diphenylphosphino)cyclohexane (tdppcy) (3) has been synthesized. Treatment of tdppcy with Mo(C$_7$H$_8$)(CO)$_3$ and Ir(PPh$_3$)$_2$(CO)Cl yields octahedral Mo(tdppcy)(CO)$_3$ (4) and trigonal-bipyramidal Ir(tdppcy)(CO)Cl (5), respectively. Compound 5 is transformed into either Ir(tdppcy)(CO)H (6) or Ir(tdppcy)(CO)(H)$_2$$^+$ (7) by treatment with NaBH$_4$ in refluxing THF. Complex 5 can be oxidized by dichloromethane or Cl$_2$ to the trichloro complex Ir(tdppcy)Cl$_3$ (8), which can be converted into the dihydride Ir(tdppcy)(H)$_2$Cl (9) by treatment with NaBH$_4$ in THF. The dynamic behavior of the highly fluxional pentacoordinate complexes 5 and 6 has been studied by VT ^{31}P{^{1}H} NMR spectroscopy. An X-ray diffraction study has been carried out on 8 · 3CH$_2$Cl$_2$.

Key words: Iridium; Molybdenum; Phosphine; Fluxionality; Nuclear magnetic resonance; Crystal structure

1. Introduction

Polydentate phosphine ligands are receiving ever-growing attention because of their rich coordination chemistry and the catalytic application of their metal complexes [1–4]. The connectivity of the backbone in the polydentate phosphines is of importance for the stereochemistry that is imposed by the ligand on the metal [5,6]. Thus with iron(II) halides P(CH$_2$CH$_2$CH$_2$PMe$_2$)$_3$ forms diamagnetic octahedral complexes of C_{2v} symmetry [5], while P(CH$_2$CH$_2$PPh$_2$)$_3$ gives low-spin paramagnetic iron complexes that are trigonal-bipyramidal and of C_{3v} symmetry [6]. We recently introduced the use of the cyclohexane ring system as a backbone in tripodal phosphine ligands [7,8]. In spite of the C_3 symmetry of those ligands, no pyramidal metal complexes have been observed for rhodium and iridium. We report here on the prepara-

tion and coordination chemistry of the new tripodal phosphine ligand *cis,cis*-1,3,5-tris(diphenylphosphino)-cyclohexane (tdppcy) (3), in which three diphenylphosphino groups are stereospecifically bound to the 1,3,5-positions of the cyclohexane ring. Upon coordination of all three phosphorus centres to a metal, a stable adamantane-type structure is formed.

2. Experimental details

2.1. General procedures

All manipulations were performed under pure argon by using Schlenk techniques. THF, toluene, and diethyl ether were freshly distilled prior to use from sodium/benzophenone, and n-hexane and dichloromethane from LiAlH$_4$. *cis,cis*-1,3,5-Cyclohexanetriol was purchased from Aldrich Chemical Co. Published methods were used for the preparation of *cis,cis*-1,3,5-cyclohexanetritosylate [9], Mo(CO)$_3$(η^6-C$_7$H$_8$) [10], and Ir(PPh$_3$)$_2$(CO)Cl [11].

Mass spectra: FD, Finnigan MAT 711 A modified by AMD; FAB, Finnigan TSQ 70. IR: Bruker IFS 48. ^{31}P{^{1}H} NMR: Bruker WP 80 and AC 80 (32.39 MHz and 32.44 MHz; ext. standard 1% H$_3$PO$_4$/acetone-d$_6$.

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* Dedicated to Prof. H. Werner on the occasion of his 60th birthday.
** X-ray structure analysis.

TABLE 1. Selected spectroscopic data for compounds 3–9

Compound	ν(CO)/ν(IrH) [cm⁻¹](KBr)	³¹P{¹H} [ppm] [a] J_{PP} (Hz)	¹³C{¹H} [ppm] [c] CH	CH₂	CO	¹H [ppm] [c] Hydrides
tdppcy (3)		−6.5 (s) [b]	36.9 (dt) [d] (10.2, 12.7)	32.2 (t) [d] (16.0)		
Mo(tdppcy)(CO)₃ (4)	1932, 1827/	22.8 (s)	28.5	27.9	221.0	
Ir(tdppcy)(CO)Cl (5)	1899/	−14.1 (s)	24.3	27.0	201.0	
Ir(tdppcy)(CO)H (6)	1889/2032	−16.2 (s)	23.4	27.9		−10.01 (q) [e]
Ir(tdppcy)(CO)(H)₂⁺ (7)	2040/2093	−17.7 (t), −26.3 (d) (22.3)	20.5 21.9	26.7 27.0	171.2	−10.02 [f]
Ir(tdppcy)Cl₃ (8)		−38.3 (s)				
Ir(tdppcy)(H)₂Cl (9)	/2067	0.6 (t), −22.2 (d) (8.6)	22.8 23.8	27.7		−8.55 [f]

[a] Unless otherwise noted the spectra were measured in CH_2Cl_2. [b] THF. [c] Measured in CD_2Cl_2, unless otherwise noted these resonances consists of complex multiplets, only the center line of the signals are listed. [d] $CDCl_3$. [e] Toluene-d_8. [f] AA' part of an AA'MXX' spectrum.

¹H and ¹³C{¹H} NMR: Bruker AC 250 (250.13 MHz and 62.90 MHz; chemical shifts were measured relative to partially deuterated solvent peaks which were referenced to tetramethylsilane. In addition to the ¹³C{¹H}NMR spectrum a ¹³C-DEPT [12] experiment was routinely recorded for each compound. ³¹P CP MAS: Bruker ASX 300. The 2D-EXSY experiment on 6 was performed with a pulse sequence supplied by Bruker. A delay of 2 s was used between aquisitions. The mixing period was selected to 4 s. ³¹P DNMR experiments were carried out on a Bruker AC 250. The temperature was measured using a temperature control unit (VT 100 Bruker instrument) and an external thermocouple (Pt 100). The NMR probe temperature was calibrated by the van Geet method [13]. The exchange-broadened NMR spectra were simulated by use of a modified version of DNMR5 [14*] available from the Quantum Chemistry Program Exchange (QCMP 365). The analysis of the rate constant data was performed with ACTPAR [15], a nonlinear least-squares program to fit the values of the desired parameters.

Selected spectroscopic data are listed in Table 1.

2.2. Synthesis of cis,cis-1,3,5-Tris(diphenylphosphino)cyclohexane (3)

An ice-cooled solution of 2.0 g (10.1 mmol) of diphenylphosphine in 20 ml of n-hexane was treated with 7.6 ml of a 1.6 M solution of ⁿBuLi/n-hexane. The yellow suspension was allowed to warm to room temperature and stirred for an additional 3 h. A suspension of 2 g (3.36 mmol) of 2 in 50 ml of THF was then added dropwise, and after 16 h stirring, the solution was treated with water, and the organic layer was separated, and dried over silica gel. The solvent was evaporated under vacuum, and the residual colorless

oil was washed with n-hexane. Additional washing with ether gave analytically pure 3 as a colorless powder. Yield 410 mg (19%), m.p. 218°C. ¹H NMR (CDCl₃, ppm): δ 1.25 (dtt, ²J(HH) = 12.5 Hz, ³J(HH) = 11.5 Hz, ³J(PH) < 5 Hz, 3H, CHH_a); 1.9 (dtt, ²J(HH) = 12.5 Hz, ³J(HH) < 4 Hz, ³J(PH) < 4 Hz, 3H, CHH_e); 2.45 (dtt, ³J(HH) = 11.5 Hz, ²J(PH) = 4.6 Hz, ³J(HH) < 4 Hz, 3H, PCH); 7.39–7.88 (m, 30H, C₆H₅). ¹³C{¹H} NMR (CDCl₃, ppm): δ 128 (d, ³J(PC) = 7 Hz, m-C₆H₅); 128.6 (s, p-C₆H₅); 133.2 (d, ²J(PC) = 18.8 Hz, o-C₆H₅); 136.2 (d, ¹J(PC) = 14.2 Hz, ipso-C₆H₅). Anal. Found: C, 79.51; H, 6.35; mol. mass. (FD): 636, C₄₂H₃₉P₃ calc.: C, 79.23; H, 6.17%.

2.3. Tricarbonyl[cis,cis-1,3,5-tris(diphenylphosphino)cyclohexane]molybdenum(0) (4)

A mixture of equimolar amounts of Mo(CO)₃(η^6-C₇H₈) (54.9 mg, 0.2 mmol) and a tdppcy (128 mg, 0.2 mmol) in 10 ml of toluene was kept at 80°C for 2 h, during which a bright yellow precipitate was formed. This was collected on a sintered class frit and washed with pentane. Yield 100 mg (60%), m.p. 281°C (dec.). ¹H NMR (CD₂Cl₂, ppm): δ 1.95 (m, 3H, CHH_a); 2.24 (m, 3H, PCH); 2.79 (m, 3H, CH_eH); 7.08–7.4 (m, 30H, C₆H₅). ¹³C{¹H} NMR (CD₂Cl₂, ppm): δ 128.2 (m, m-C₆H₅); 129.4 (s, p-C₆H₅); 133.0 (m, o-C₆H₅); 138.0 (m, ipso-C₆H₅). Anal. Found: C, 65.42; H, 4.85; mol. mass. (FD): 817, C₄₅H₃₉MoO₃P₃ calc.: C, 66.18; H, 4.81%.

2.4. Carbonylchloro[cis,cis-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(I) (5)

A mixture of equimolar amounts of Ir(PPh₃)₂(CO)Cl (141.6 mg, 0.18 mmol) and tdppcy (115.6 mg, 0.18 mmol) in toluene was kept at 80°C for 3 h. The orange precipitate was filtered off and washed with pentane. Yield 115 mg (96%), m.p. 179°C (dec). ¹H NMR

$(CD_2Cl_2$, ppm): δ 2.28 (m, 3H, CHH_a); 2.47 (m, 3H, PCH); 3.19 (m, 3H, CH_eH); 7.04-7.49 (m, 30H, C_6H_5). $^{13}C\{^1H\}$ NMR $(CD_2Cl_2$, ppm): δ 128.1 (m, m-C_6H_5); 129.5 (s, p-C_6H_5); 132.9 (m, o-C_6H_5); 133.9-135.3 (m, $ipso$-C_6H_5). ^{31}P CP MAS NMR: δ -5.41 (s, 1P, P_{ap}); -19.55 (s, 2P, P_{eq}). Anal. Found: C, 57.91; H, 4.44; Cl, 3.99; mol. mass. (FD) 892.3, $C_{43}H_{39}ClIrOP_3$ calc.: C, 57.88; H, 4.40; Cl, 3.97%.

2.5. Carbonylhydrido[cis,cis-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(I) (6)

A suspension of 100 mg Ir(tdppcy)(CO)Cl (5) (0.1 mmol) and 8 mg (0.2 mmol) of $NaBH_4$ in THF was refluxed for 1 h, the mixture was then allowed to cool to room temperature. The NaCl and excess of $NaBH_4$ were removed and the solvent was than evaporated off under reduced pressure. The residue was recrystallized from hot toluene. Yield 73 mg (76%), m.p. 162°C (dec.). ^1H NMR (toluene-d_8, ppm): δ 1.8-2.3 (m, 6H, CHH_a and PCH); 2.9 (m, 3H, CH_eH); 6.7-7.7 (m, 30H, C_6H_5). $^{13}C\{^1H\}$ NMR (toluene-d_8, ppm): δ 124.6-133.5 (m, C_6H_5). Anal. Found: C, 59.85; H, 4.63; mol. mass. (FD) 858.3, $C_{43}H_{40}IrP_3$ calc.: C, 60.20; H, 4.70%.

2.6. Carbonyldihydrido[cis,cis-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(III)-hexafluorophosphate (7)

2.6.1. Method A

A suspension of 47 mg (0.05 mmol) of 5 and 4 mg (0.1 mmol) of $NaBH_4$ in THF (10 ml) was heated under reflux for 2 h, and then cooled to 0°C. The mixture was hydrolyzed and the organic layer separated and dried over silica gel. After evaporation of the solvent the crude product was stirred with 180 mg (1.2 mmol) of NH_4PF_6 in methanol for 12 h, the remaining NH_4PF_6 was filtered off, and the solvent removed under reduced pressure. Product 7 was extracted with 30 ml of dichloromethane, and recrystallized from $CHCl_3$. Yield 17.4 mg (40%), m.p. 165°C (dec.). ^1H NMR $(CD_2Cl_2$, ppm): δ 2.24 (m, 3H, CHH_a); 2.83 (m, 3H, PCH); 3.37 (m, 3H, CH_eH); 7.07-7.45 (m, 30H, C_6H_5). $^{13}C\{^1H\}$ NMR $(CD_2Cl_2$, ppm): δ 128.2-134.5 (m, C_6H_5). Anal. Found: C, 51.23; H, 4.05; F, 19.21; mol. mass (FD) 859.5 (cation only), $C_{43}H_{41}F_6IrOP_4$ calc.: C, 51.45; H, 4.12; F, 19.15%.

2.6.2. Method B

A mixture of 100 mg (0.12 mmol) of 6 and 20 mg of NH_4PF_6 in 20 ml of toluene was stirred at room temperature for 16 h. The solvent was removed in vacuo, and the residue was recrystallized from $CHCl_3$. Yield 93 mg (77%).

TABLE 2. Crystal data and summary of intensity data collection and structure refinement of 8

Empirical formula	$C_{45}H_{45}Cl_9IrP_3$
Formula weight	1190.0
Space group	Pbca
Unit cells dimensions a	2237.2(11) pm
b	1725.0(6) pm
c	2443.3(8) pm
Volume	$9429(6) \times 10^6$ pm^3
Density (calc.)	1.677 g cm^{-3}
Z	8
F(000)	4720
Temperature (K)	173
Radiation	Mo-Kα
μ(Mo-Kα)	3.477 mm^{-1}
2θ Range	4-50°
Scan Type	ω
Scan Speed	Variable; 7.32 to 29.30° min^{-1} in ω
h	$-26 \to 26$
k	$-20 \to 5$
l	$-29 \to 29$
Reflections collected	21475
No. of unique data with $I > 2\sigma I$	4591
No. of parameters refined	268
R	0.074
R_w	0.069

2.7. Trichloro[cis,cis-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(III) (8)

Chlorine was bubbled through a solution of 308 mg (0.34 mmol) of 5 in 40 ml of dichloromethane until a colorless solid began to precipitate out (1 h). After 16 h heating under reflux, the mixture was concentrated to 10 ml and the colorless precipitate was filtered off and washed with dichloromethane and pentane. Yield 224 mg (70%), m.p. 156°C (dec.). ^1H NMR $(CD_2Cl_2$, ppm): δ 2.35 (m, 3H, CHH_a); 2.52 (m, 3H, PCH); 3.08 (m, 3H, CH_eH); 7.10-7.80 (m, 30H, C_6H_5). Because of the poor solubility, no $^{13}C\{^1H\}$ NMR spectrum with an adequate signal-to-noise ratio could be obtained. The elemental analysis was performed on an amorphous sample which had been dried in vacuo. Anal. Found. C, 53.22; H, 4.19; Cl, 12.03; mol. mass. (FAB) 899.1 (M$^+$- Cl), $C_{42}H_{39}Cl_3IrP_3$ calc.: C, 53.94; H, 4.20; Cl 11.37%.

2.7.1. X-ray structure determination of 8 [16*]

Colorless crystals of 8 were obtained by crystallization from dichloromethane. A suitable crystal with approximate dimensions 0.15 × 0.2 × 0.3 mm was mounted on a glass fiber which was transfered to a Siemens P4 diffractometer. The final cell parameters and specific data collection parameters for 8 are summarized in Table 2. The structure was solved by the Patterson method [17]. All non-hydrogen atoms except

those for the solvent molecules were refined anisotropically. The hydrogen atoms were placed at calculated positions. Three molecules of CH_2Cl_2 were located in the asymmetric unit. Final atomic positional parameters for **8** are listed in Table 3.

2.8. Chlorodihydrido[cis,cis-1,3,5-tris(diphenylphosphino)cyclohexane]iridium(III) (9)

Solid $NaBH_4$ (120 mg, 3.2 mmol) was added to a well-stirred suspension of **8** (280 mg, 0.3 mmol) in 20 ml of THF. The mixture was heated under reflux for 6 h, the suspension was cooled to 0°C and hydrolyzed. The organic layer was separated and dried with silica gel. Concentration of the solution to 3 ml and addition of n-hexane (10 ml) gave colorless crystals which were filtered off, washed with pentane, and dried *in vacuo*. Yield 180 mg (69%), m.p. 144°C (dec.). ^1H NMR (CD_2Cl_2, ppm): δ 2.0–2.8 (m, 6H, CHH_a, PCH); 3.24 (m, 3H, CH_eH); 6.9–7.3 (m, 30H, C_6H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, ppm): δ 127.5–135.5 (m, C_6H_5). Anal. Found: C, 57.84; H, 4.98; Cl, 3.79; mol. mass. (FAB) 864.2, $C_{42}H_{41}ClIrP_3$ calc.: C, 58.23; H, 4.77; Cl, 4.09%.

3. Results and discussion

3.1. Synthesis and characterization of cis,cis-1,3,5-tris-(diphenylphosphino)cyclohexane (3)

cis,cis-1,3,5-Tris(diphenylphosphino)cyclohexane (3) has been prepared by a two-step procedure from cis,cis-1,3,5-cyclohexanetriol (1) (Scheme 1). The tosylate 2 has been described previously [9]. Treatment of 2 with a slight excess of $LiPPh_2$ in an n-hexane/THF mixture gave 3 as a colorless solid in yields not exceeding 20%. The poor yields are caused by side reactions that compete with the nucleophilic displacement of the tosylate anion by diphenylphosphide [18]. Because of the steric hindrance at the α–C atom in 2 and the increased acidity of the ring methylene hydrogens, the basic character of the diphenylphosphide becomes more important. This leads to a complicated product mixture that contains, among other species, diphenylphosphine and tdppcy [18,19]. Nevertheless 3 can be easily isolated from the oily product mixture by a simple washing procedure (see Experimental details).

The conformation, and thus the connectivities, in tdppcy, was established by ^1H, ^{13}C, and ^{31}P NMR spectroscopy (Table 1). In the alkane region of the $^{13}C\{^1H\}$ NMR spectrum only one signal is observed for each of the methine (δ 36.9) and methylene (δ 32.2) groups of the cyclohexane ring. Both resonances are split by the interaction with the phosphorus nuclei to a doublet of triplets and a triplet, respectively. In the ^1H

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$ A^2) for **8**

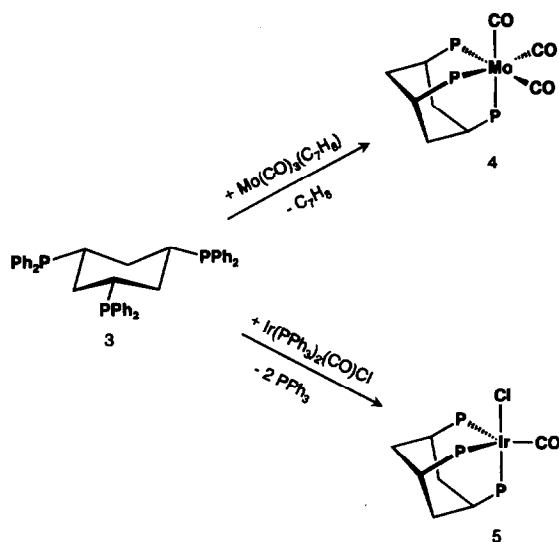| Atom	x	y	z	U_{eq}
Ir(1)	368(1)	2405(1)	2353(1)	23(1)
Cl(1)	662(3)	1136(3)	2698(3)	64(2)
Cl(2)	−158(2)	1619(2)	1703(2)	39(1)
Cl(3)	1218(3)	2109(3)	1770(2)	58(2)
P(1)	343(2)	2516(2)	3017(1)	24(1)
P(2)	1017(2)	3139(2)	2887(2)	26(1)
P(3)	26(2)	3506(2)	1924(2)	25(1)
C(1)	−465(7)	3530(9)	3243(6)	27(3)
C(2)	93(7)	3813(10)	3562(6)	29(3)
C(3)	640(7)	3991(9)	3188(6)	28(4)
C(4)	441(8)	4568(9)	2736(6)	36(4)
C(5)	−98(7)	4300(9)	2404(6)	27(3)
C(6)	−625(7)	4109(9)	2792(6)	28(4)
C(8)	−714(10)	2130(12)	4060(8)	51(5)
C(9)	−715(12)	1783(14)	4577(11)	72(7)
C(10)	−205(11)	1366(15)	4727(10)	67(6)
C(11)	235(12)	1277(15)	4382(10)	73(7)
C(12)	227(9)	1611(11)	3861(8)	46(5)
C(13)	−255(7)	2059(9)	3698(6)	29(3)
C(14)	−1610(7)	2560(10)	2879(6)	36(3)
C(15)	−2132(8)	2195(10)	2764(6)	35(4)
C(16)	−2155(8)	1415(10)	2617(7)	40(4)
C(17)	−1632(8)	993(10)	2583(7)	40(4)
C(18)	−1102(7)	1357(8)	2701(6)	28(3)
C(19)	−1072(7)	2121(9)	2853(6)	28(3)
C(20)	1711(7)	1968(10)	3332(7)	33(4)
C(21)	2008(9)	1588(12)	3748(7)	45(4)
C(22)	2009(9)	1872(12)	4282(8)	51(5)
C(23)	1720(8)	2538(12)	4376(8)	50(4)
C(24)	1393(8)	2936(10)	3975(7)	37(4)
C(25)	1381(7)	2651(10)	3463(6)	32(3)
C(26)	1767(8)	3721(10)	2023(7)	37(4)
C(27)	2269(9)	4133(11)	1840(8)	43(4)
C(28)	2668(8)	4458(11)	2215(7)	40(4)
C(29)	2595(8)	4358(11)	2757(7)	41(4)
C(30)	2089(7)	3934(10)	2941(8)	35(4)
C(31)	1680(7)	3622(8)	2582(6)	27(3)
C(32)	−816(8)	4164(10)	1229(7)	38(4)
C(33)	−1331(9)	4222(12)	933(8)	51(5)
C(34)	−1768(9)	3639(12)	964(8)	48(5)
C(35)	−1652(9)	3023(11)	1298(7)	46(4)
C(36)	−1120(8)	2945(10)	1591(7)	36(4)
C(37)	−682(8)	3498(10)	1550(7)	38(4)
C(38)	688(7)	3376(10)	980(7)	33(4)
C(39)	1060(9)	3628(11)	577(8)	43(4)
C(40)	1262(10)	4362(13)	552(9)	60(6)
C(41)	1089(9)	4878(12)	939(8)	51(5)
C(42)	700(8)	4661(10)	1371(7)	40(4)
C(43)	513(7)	3874(10)	1392(7)	34(4)
Cl(4)	6453(5)	6511(7)	147(4)	131(3)
Cl(5)	6672(6)	5264(7)	875(4)	139(4)
C(7)	6138(21)	5959(26)	649(17)	144(15)
Cl(6)	2571(6)	2461(8)	747(5)	150(4)
Cl(7)	2473(7)	857(8)	445(5)	159(4)
C(7A)	2530(26)	1545(26)	899(18)	162(17)
Cl(8)	4592(9)	6487(13)	145(8)	228(8)
Cl(9)	3935(10)	4976(12)	728(8)	232(8)
C(7B)	4548(15)	5209(18)	375(13)	96(9)
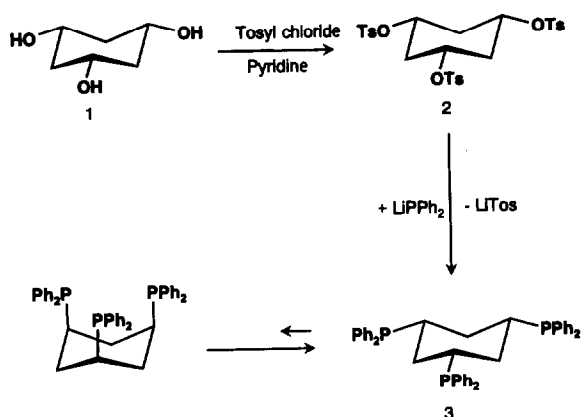
Scheme 1.

Scheme 2.

NMR spectrum the inequivalent ring hydrogens give rise to three multiplet patterns that are consistent with a chair conformation of the cyclohexane ring with the three diphenylphosphine goups in the equatorial positions [20]. This is consistent with a C_{3v} symmetry of the ligand, which is supported by the observation of only one signal in the $^{31}P\{^1H\}$ NMR spectrum.

3.2. Complexation

If in 3 inversion of the cyclohexane ring occurs, so that the three functional groups are located at the axial positions (Scheme 1), the donating electron pairs of the phosphorus atoms point towards the C_3 axis and would be expected to coordinate *facially* to an octahedral metal complex. That this is the case, was demonstrated by treating tdppcy with $Mo(CO)_3(\eta^6\text{-}C_7H_8)$, where 3 readily displaces the cycloheptatriene to give 4 as a bright yellow solid (Scheme 2). The two $\nu(CO)$ absorptions in the IR (KBr) spectrum, at 1932 and 1827 cm^{-1}, respectively, are typical for an octahedral tricarbonyl complex of C_{3v} symmetry [21,22]. This is consistent with the *facial* coordination of tdppcy. The high symmetry of the molecule is also reflected in the ^1H, ^{13}C, and ^{31}P NMR spectra. Three broad multiplets are observed for the inequivalent ring hydrogen atoms in the ^1H NMR spectrum, two multiplet patterns for the ring methine and methylene groups in the alkane region of the $^{13}C\{^1H\}$ NMR spectrum, and only one phosphine $^{31}P\{^1H\}$ NMR resonance (Table 1). When *facial* coordination of tdppcy to a metal fragment, occurs in the resulting complexes the coordination center is tied into an adamantane-type structure.

3.3. Synthesis and reactivity of Ir(tdppcy)(CO)Cl (5)

When $Ir(PPh_3)_2(CO)Cl$ is treated with an equimolar amount of tdppcy in toluene at 80°C, a bright orange powder is obtained, and from spectroscopic data this was formulated as Ir(tdppcy)(CO)Cl (5) (Scheme 2).

Complex 5 is soluble in dichloromethane but reacts with it at room temperature within two weeks to yield 8, along with two other products that have not been identified. The new pentacoordinate complex Ir(tdp-pcy)(CO)Cl (5) also decomposes in the solid state at room temperature during several days even when kept under argon. A suspension of 5 in refluxing THF reacts with $NaBH_4$ to give the five-coordinate complex Ir(tdppcy)(CO)H (6), which was isolated as a bright
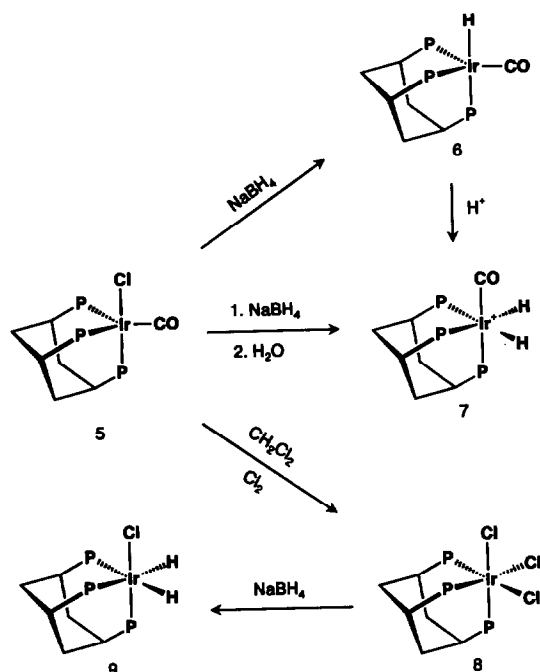
Scheme 3.

yellow solid (Scheme 3). Solutions of 6 in rigorously dry THF and toluene are stable for days, but the complex reacts with dichloromethane at room temperature within minutes to give several products that have not been identified. The pentacoordinate hydride (6) behaves as a strong base and is readily protonated by the weak acid NH_4PF_6 to give the octahedral cation Ir(tdp-pcy)(CO)H_2^+ (7). The colorless cation 7 can be isolated as its PF_6^- salt. The complex Ir(tdppcy)(CO)Cl (5) is oxidized by dichloromethane to the octahedral trichloro complex 8 within two weeks. The complex Ir(tdppcy)Cl$_3$ (8) can also be obtained by the method reported for the synthesis of Ir(tdpme)Cl$_3$ (tdpme = MeC(CH$_2$PPh$_3$)$_3$) [23] (Scheme 3). The reduction of 8 with NaBH$_4$ in boiling THF gives exclusively the dihydride 9. No monohydride or trihydride was observed during the course of the reaction. The colorless air stable compound 8 and the colorless dihydride 9 dissolve sparingly in dichloromethane and THF.

3.4. Spectroscopic characterization

Owing to the high electron density at the metal center, which is caused by the coordination of all three phosphine groups to iridium, the carbonyl absorption in the IR spectra of 5 (1899 cm^{-1}) and 6 (1889 cm^{-1}) (Table 1) are rather low. As expected ν(CO) in Ir(tdp-pcy)(CO)H_2^+ (7) is shifted to higher frequencies (2040 cm^{-1}) [24–28]. The ν(Ir–H) of 6, 7 and 9 appear in the range of 2032–2093 cm^{-1}, and are typical for hydrogen trans to a strong trans-influence ligand [26].

Pentacoordinate d^8 metal complexes are stereochemically non-rigid [24,25,27], and either a square pyramid or a trigonal bipyramid is expected as the ground state geometry. The stereochemical constraints in tdppcy require a facial arrangement at the metal center, and thus ^{31}P NMR spectroscopy is able to distinguish unambiguously between the two geometrical isomers in cases where the flexibility is lower [24,27]. The ^{31}P{^{1}H} NMR spectra of 5 and 6 at room temperature display sharp singlets at δ −14.1 and −16.2, respectively, which is consistent with high fluxionality. Upon off-resonance decoupling, the signal of 6 is split into a doublet by the interaction of the phosphorus nuclei with a single hydride. When the temperature is lowered the signal of 5 remains sharp until below −50°C the lineshape gradually broadens, indicating that the exchange process is slowed down. Even at the lowest accessible temperature (−100°C) no decoalescence is observed. In contrast, when a solution of 6 in toluene is cooled, the line becomes broader, until at −62°C the coalescence point is reached (Fig. 1). Further cooling below −96°C reveals a doublet at δ −16.3 (^2J(PP) = 20.8 Hz) and a triplet at δ −21.8 (^2J(PP) = 20.8 Hz) corresponding to a trigonal-bipyramidal

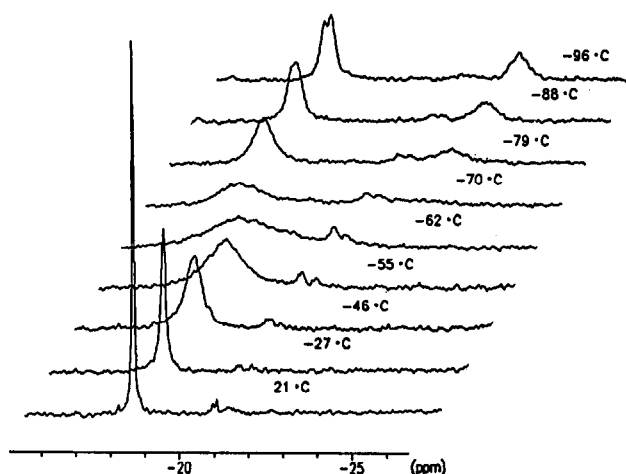

Fig. 1. Variable-temperature ^{31}P{^{1}H} NMR spectra of 6.

ground state structure [24]. Thus the barrier to pseudo-rotation in 6 is higher than that in 5, but both are lower than those observed in related five-coordinate complexes of the type M(tdpme)(CO)X (M = Rh, Ir; X = Cl, H, alkyl) with the tridentate phosphine ligand MeC(CH$_2$PPh$_2$)$_3$ (tdpme) [24,25,27,28]. A modified version of DNMR5 [14] has been used to study the mutual exchange of the three phosphorus nuclei. Graphic application of the Eyring equation to the kinetic data involving a non-linear least-square program (ACTPAR [15]) afforded the thermodynamic parameters $\Delta H^{\#}$ (21.3 ± 2 kJ mol^{-1}), $\Delta S^{\#}$ (−0.1 ± 0.01 kJ mol^{-1} K^{-1}), and $\Delta G^{\#}$ (38.8 kJ mol^{-1}). The near zero value of $\Delta S^{\#}$ is consistent with an ordered transition state and an intramolecular exchange process.

The room-temperature solid-state ^{31}P CP MAS NMR spectrum of Ir(tdppcy)(CO)Cl (5) displays two resonances at δ −5.4 and −19.6 with an integration ratio of 1:2. This is also consistent with a trigonal bipyramidal ground state structure, and is consistent with the results of an X-ray study performed on Ir(tdpme)(CO)Cl which established that in the solid state the trigonal-bipyramidal geometry with CO occupying an equatorial site is preferred [25]. That the exchange process between the equatorial and the axial phosphine sites is still operative in the solid state was demonstrated by the ^{31}P CP MAS 2D EXSY NMR spectrum [29] (Fig. 2). The appearence of the cross peaks between the two resonances results from exchange between the equatorial and axial site.

In accord with the stronger trans influence of the hydrides, the two phosphine groups trans to the hydrogen ligands in 7 and 9 are observed as doublets at higher field (−26.3 ppm, ^2J(PP) = 22.3 Hz (7) and −22.2 ppm, ^2J(PP) = 8.6 Hz (9)) than the phosphine groups trans to CO and chloride, which give rise to

triplets at δ -17.7 ($^2J(PP) = 22.3$ Hz) (7) and 0.6 ($^2J(PP) = 8.6$ Hz) (9). The assignments were supported by off-resonance decoupled ^{31}P NMR spectroscopy.

The high fluxionality in solution at room temperature accounts for the fact that only one methylene and one methine multiplet appear in the $^{13}C\{^1H\}$ NMR spectra of 5 and 6 and three broad multiplets in the alkane region of the ^1H NMR spectra (Table 1). In addition 5 displays a quartet at δ -10.01 ($J(PH) = 21.24$ Hz) because of the hydride ligand. Lowering the temperature causes the center lines of the hydride multiplet first to broaden then to collapse. At the lowest accessible temperature ($-100°C$) the multiplet coalesces into the baseline.

The hydride region in the ^1H NMR spectrum of 7 and 9 contain the XX' part of an AA'MXX' spin system, centered at δ -10.02 and -8.55, which is typical for two chemically but not magnetically equivalent hydride ligands [25,30,31] (Table 1).

An X-ray structure analysis was performed on crystals of 8 grown from solution in dichloromethane. The observed molecular structure is shown in Fig. 3, and establishes the connectivities of the atoms. The cyclohexane ring exists in an almost ideal chair conformation, as is demonstrated by an average torsional angle of $\pm54.1°$ compared with $\pm55°$ in cyclohexane [32,33]. Owing to the cis,cis arrangement and the triaxial orientation of the diphenylphosphine groups, the tdppcy ligand adopts a facial coordination at the metal center, and thus locks the framework to an adamantane-like structure. Three chlorine ligands complete the octahedral environment around iridium. The P–Ir–P angles fall within the typical narrow range 89.4(1)–91.0(1)
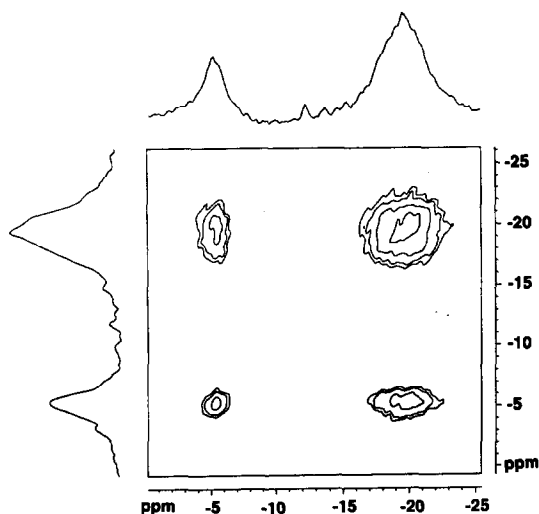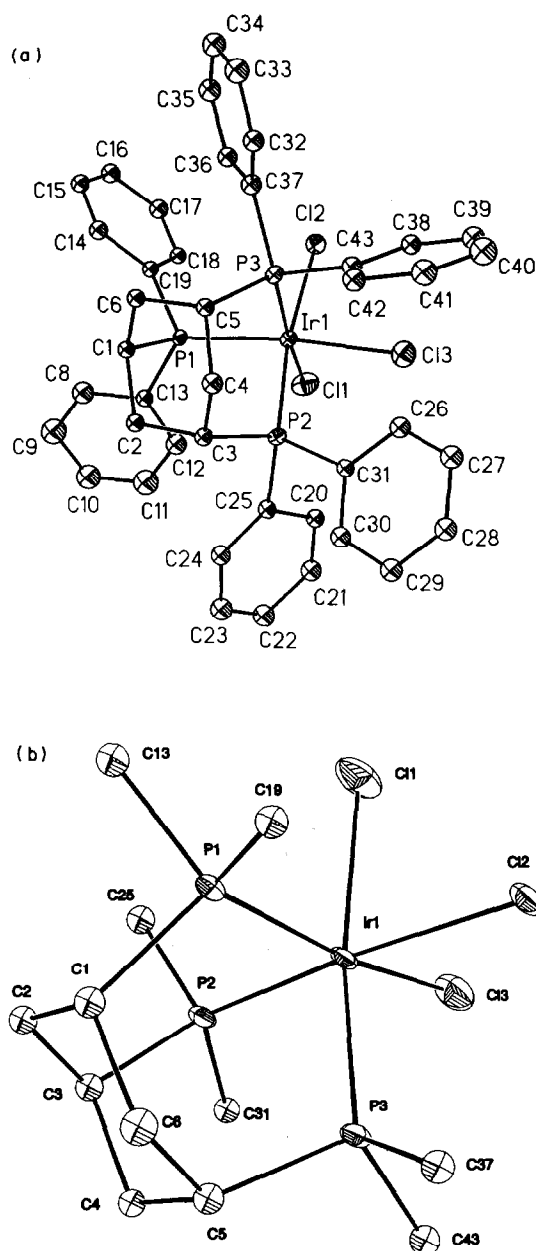

Fig. 3. (a) ORTEP plot of 8. Selected bond distances (pm), bond angles (°) and torsional angles (°): Ir1–Cl1 242.6(5), Ir1–Cl2 241.7(5), Ir1–Cl3 239.8(6), Ir1–P1 230.8(4), Ir1–P2 230.1(4), Ir1–P3 231.4(4), Cl1–Ir–Cl2 81.4(2), Cl1–Ir1–Cl3 79.4(2), Cl2–Ir1–Cl3 83.2(2), P1–Ir–P2 89.4(1), P1–Ir–P3 90.3(1), P2–Ir–P3 91.0(1), C1–C2–C3–C4 $-54.6(2)$, C2–C3–C4–C5 $-54.6(2)$, C3–C4–C5–C6 54.8(2), C4–C5–C6–C1 $-53.81(2)$; (b) only ipso carbon atoms of the phenyl rings are shown for clarity.

[1,34], while the Cl–Ir–Cl angles deviate slightly from the ideal octahedral values.

4. Conclusion

The tendency of the pentacoordinate adamantane-like complexes 5 and 6 to form octahedral compounds

Fig. 2. Room temperature 2D CP/MAS ^{31}P EXSY NMR spectrum of 5.

is demonstrated by the case with which they are oxidized or protonated. This is a result of the unfavourable distribution of the P–Ir–P angles (90°, 120°, 90°) in the trigonal-bipyramidal geometry for tdppcy, which because of its stereochemistry, prefers three P–M–P angles close to 90°. In particular the angle between the equatorial phosphines has been shown to be strongly distorted from the idealized angle of 120° to 85.7° for Ir(tdpme)(CO)Cl [25] and in the case of Rh(tdpme)(CO)Me [28] to 90.8°. To explain the reactivity pattern of the latter complex it has been argued that the angle strain can be released by the dissociation of a phosphine arm to form a square-planar rhodium complex with a six-membered ring [28]. The steric constraint of the cyclohexane backbone in tdppcy does not allow dissociation of only one phosphine group while the other two remain coordinated. Thus the only way to avoid angle strain in trigonal-bipyramidal complexes of 5 and 6 is to increase the coordination number and form octahedral complexes in which all three P–M–P angles are close to 90°.

Acknowledgments

References and notes

1 F.A. Cotton and B. Hong, Progr. Inorg. Chem., 40 (1993) 179.
2 W. Levason, in S. Patai and F.R. Hartley (eds.), The Chemistry of Organophosphorus Compounds, 1 (1990) 567.
3 L. Sacconi and F. Mani, in G.A. Nelson and B.N. Figgs (eds.), Transition Met. Chem., 8 (1982) 179.
4 C. Bianchini, A. Meli, M. Peruzzini, F. Vizza and F. Zanobini, Coord. Chem. Rev., 120 (1992) 193.
5 M. Antberg and L. Dahlenburg, Inorg. Chim. Acta, 104 (1985) 51.
6 C. Bianchini, F. Laschi, D. Masi, F.M. Ottaviani, A. Pastor, M.

Peruzzini, P. Zanello and F. Zanobini, J. Am. Chem. Soc., 115 (1993) 2723.
7 H.A. Mayer and W.C. Kaska, Chem. Ber., 123 (1990) 1827.
8 H.A. Mayer, R. Fawzi and M. Steimann, Chem. Ber., 126 (1993) 1341.
9 H. Stetter and K.-H. Steinacker, Chem. Ber., 85 (1952) 451.
10 G. Brauer, Handbuch der Präparativen Anorganischen Chemie, Bd III, F. Enke Verlag, Stuttgart, 1981, p. 1885.
11 Loc. cit. 10 (1981) p. 2010.
12 R. Benn and H. Günther, Angew. Chem., 95 (1983) 381; Angew. Chem., Int. Ed. Engl., 22 (1983) 350.
13 A.L. van Geet, Anal. Chem., 42 (1970) 679.
14 The routines of data input and data conversion were modified by Hartwig Kühbauch, Universität Tübingen.
15 G. Binsch and H. Kessler, Angew. Chem., 92 (1980) 445; Angew. Chem., Int. Ed. Engl., 19 (1980) 411.
16 Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57417, the names of the authors, and the journal citation.
17 G.M. Sheldrick, SHELXTL-PC, University of Göttingen.
18 W. Wolfsberger, Chem.-Ztg., 115 (1991) 7.
19 W. Wolfsberger, Chem.-Ztg., 112 (1988) 379.
20 H. Günther, NMR-Spektroskopie, G. Thieme Verlag, Stuttgart, 1992.
21 E.W. Abel, M.A. Bennett and G. Wilkinson, J. Chem. Soc., (1959) 2323.
22 A.A. Chalmers, J. Lewis and R. Whyman, J. Chem. Soc., (1967) 1817.
23 W.O. Siegel, S.I. Lapporte and I.P. Collman, Inorg. Chem., 10 (1971) 2158.
24 L. Dahlenburg and F. Mirzaei, Inorg. Chim. Acta, 97 (1985) L1.
25 P. Janser, L.M. Venanzi and F. Bachechi, J. Organomet. Chem., 296 (1985) 229.
26 L. Vaska, J. Am. Chem. Soc., 88 (1966) 4100.
27 G.G. Johnston and M.C. Baird, Organometallics, 8 (1989) 1894.
28 E.G. Thaler, K. Folding and K.G. Caulton, J. Am. Chem. Soc., 112 (1990) 2664.
29 J. Jeener, H.B. Meier, P. Bachmann and R.R. Ernst, J. Chem. Phys., 71 (1979) 4546.
30 P. Barbaro, C. Bianchini, A. Meli, M. Peruzzini, A. Vacca and F. Vizza, Organometallics, 10 (1991) 2227.
31 C. Bianchini, P. Barbaro, A. Meli, M. Peruzzini, A. Vacca and F. Vizza, Organometallics, 12 (1993) 2505.
32 R.A. Wohl, Chimia, 18 (1964) 219.
33 M. Davis and O. Hassel, Acta Chem. Scand., 17 (1963) 1181.
34 C. Bianchini, C. Mealli, A. Meli and L. Sacconi, Inorg. Chim. Acta, 37 (1979) L543.