Trimeric Iridium(I) and Iridium(III) Complexes with the Tripodal Phosphane *cis,cis*-1,3,5-Tris[(diphenylphosphanyl)methyl]cyclohexane (tdppmcy) as Bridging Ligand☆

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Treatment of *cis,cis*-1,3,5-tris[(diphenylphosphanyl)methyl]cyclohexane (tdppmcy) (**1**) with $Ir(PPh_3)_2(CO)Cl$ in toluene gives the trinuclear complex $[Ir(CO)Cl]_3(tdppmcy)_2$ (**2**) in high yield. In this complex the tripodal molecule tdppmcy behaves as a trismonodentate ligand since each phosphorus atom is bound to one metal center. Compound **2** can be transformed into the trinuclear complexes $\{[Ir(CO)(Cl)H]_3(tdppmcy)_2\}^{3+}$ (**3**), $[Ir(CO)(Cl)H_2]_3(tdppmcy)_2$ (**4**), and $[Ir(CO)H_3]_3(tdppmcy)_2$ (**5**) by treatment with H^+, H_2, and H^-, respectively. The chemistry of **2** supports the spectroscopic findings of a square-planar environment at the metal centers in **2**.

The excellent ligating properties of tertiary phosphanes have made them important constituents of compounds used for catalysis[1], study of structure-bonding relationships, and spectroscopic studies[2]. In this context, polyphosphanes have been developed to improve the stability and to control the stereochemistry and reactivity of transition metal complexes[3,4]. Polyphosphanes can act as both chelating and bridging ligands, depending on the design of the backbone. In general, the thermodynamic advantage of the chelate effect favors the formation of five- and six-membered rings as compared to the bridging mode. If the bite angle becomes small the bridging mode is observed as well as four-membered rings. If the ring size becomes larger (>7) the bridging mode is preferred[5]. Although the C_3 symmetry of the ligands should generate pyramidal metal complexes, the use of the cyclohexane ring as backbone in tripodal phosphane ligands results in different coordination behavior[6–8]. We report here on the coordination chemistry of the tripodal phosphane ligand *cis,cis*-1,3,5-tris[(diphenylphosphanyl)methyl]cyclohexane (tdppmcy)[6] (**1**) which forms trinuclear iridium complexes.

Trimeric Iridium Complex 2

Treatment of $Ir(PPh_3)_2(CO)Cl$ with the potentially tripodal phosphane ligand *cis,cis*-1,3,5-tris[(diphenylphosphanyl)methyl]cyclohexane (tdppmcy) (**1**) in a stoichiometric ratio of 3:2 in hot toluene gives the trinuclear tris(carbonylchloroiridium) complex **2** in high yield (Scheme 1). The composition of **2** has been established by elemental analysis, mass spectrometry, and molecular mass studies. The molecule consists of two tdppmcy (**1**) ligands held together by three bridging iridium atoms. Each of the three metal centers is *trans*-coordinated by two diphenylphosphanyl groups of two different tdppmcy ligands, one chlorine and one carbonyl ligand in a square-planar way. The stereochemistry around the coordination centers is thus the same as in Vaska's complex $Ir(PPh_3)_2(CO)Cl$[9]. This is nicely demonstrated by their IR spectra. The ν(CO) absorption at 1957 cm^{-1} of **2** differs from Vaska's complex by only 7 wave numbers. It is observed at a higher energy (>60 wave numbers) than would be expected if all three phosphane groups of one tdppmcy ligand are connected to the same metal center[8,10].

The number of the resonances in the ^1H-, ^{13}C-, and ^{31}P-NMR spectra are in agreement with a C_3 symmetry of the trimeric iridium complex **2** (Table 1). Thus, the $^{31}P\{^1H\}$-NMR spectrum displays a singlet at δ 21.7 while the $^{13}C\{^1H\}$-NMR spectrum shows three signals in the alkane region which can be assigned to the ring methylene, the methine, and the methylene groups bound to the phosphorus atoms. Evidence for two mutually *trans*-coordinated phosphane ligands is given by the multiplet pattern of the CH_2P groups. At δ 33.9 a triplet is observed with an intensity ratio of almost 1:2:1 consistent with an AXX′ spin system ($A = {}^{13}C$; $X,X' = {}^{31}P$)[11] caused by the interaction of the CH_2P group with two phosphorus nuclei via one and two bonds, respectively ($CH_2P-Ir-P$). The observed virtual triplet indicates a $|{}^2J_{PP}|$ value larger than 50 Hz which is the case when the phosphane ligands in question are positioned *trans* (Table 1)[12,13]. The multiplicities of the resonances due to the axial hydrogens of the cyclohexane rings in the alkane region of the ^1H-NMR spectrum are in agree-

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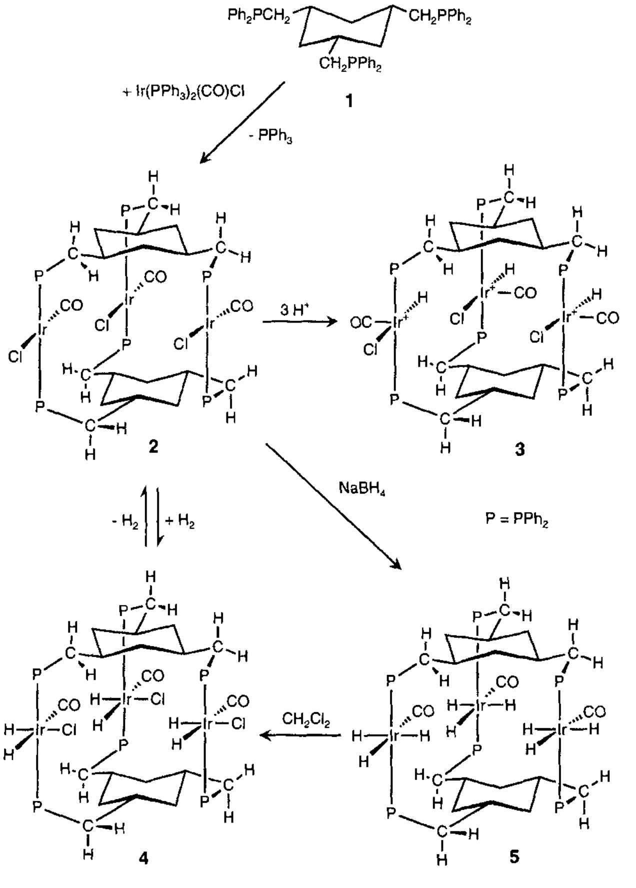
ment with a chair conformation of the cyclohexane ring. The diastereotopic geminal hydrogen atoms of the CH_2P groups give rise to two broad multiplets at δ 2.2 and 2.8 which is also consistent with a C_3 symmetry of the molecule.

Scheme 1



From molecular modelling studies[14] the average distance between each two iridium atoms is estimated to be greater than 6 Å. This is comparable to distances which have been obtained by a single-crystal X-ray structure analysis of the trimeric Ni(II) complex $[Ni_3Cl_6(etp)_2]$ (etp = 1,1,1-tris[2-(diphenylphosphanyl)ethyl]ethane)[15]. Isomers which might be caused by hindered rotation of the Cl–Ir–CO moieties have not been observed.

Reactivity of 2 with H^+, H_2, and H^-

The square-planar geometry of the metal centers in the trinuclear tris(carbonylchloroiridium) complex **2** is also documented in its reactivity towards protons, hydrogen, and hydrides (Scheme 1).

Treatment of an intense yellow solution of **2** in dichloromethane with a slight excess of HSO_3CF_3 results in the formation of the colorless trication **3** within minutes (Scheme 1). An anion metathesis with $NaBPh_4$ is prevented due to the high acidity of the iridium cations; the starting material **2** is recovered quantitatively.

Kinetically controlled formation of the *cis* hydrido product[16] **4** is completed under one atmosphere of hydrogen at room temperature within two hours by oxidative addition of H_2 to **2**. Chiral centers are generated at the three iridium atoms due to the coordination of H_2. Therefore, four pairs of diastereomers result which can be recognized in the NMR spectra as partly overlapping multiplets. However, after recrystallization the final compound consists entirely of one isomer, and spectroscopy has been performed on this species (see below). The quantitative reductive elimination of H_2 from **4** upon warming demonstrates the reversibility of the addition reaction (Scheme 1).

The reduction of the tris(carbonylchloroiridium) complex **2** with an excess of $NaBH_4$ in THF affords the pale yellow tris(trihydridoiridium) complex **5** in almost quantitative yield according to the ^{31}P-NMR spectrum. The stereochemical control of the tripodal phosphane ligand tdppmcy allows the exclusive formation of the *mer* derivative. This is in contrast to Vaska's complex $Ir(PPh_3)_2(CO)Cl$ which under the same conditions gives a mixture of the *fac* and *mer* isomers[17]. When a stoichiometric (3:1) amount of $LiBEt_3H$ is used the only new product which has been isolated is **5**, while the bulk of **2** does not react. As for the $Ir(PPh_3)_2(CO)Cl$ complex, **2** cannot be transformed to the highly unstable monohydride[18]. The air-stable tris(trihydridoiridium) complex **5** decomposes in the solid state at room temperature within days but it can be stored below −30°C for weeks. Complex **5** is soluble in THF, toluene, and dichloromethane. In the latter solvent **5** reacts to give the tris(carbonylchlorodihydrido) complex **4** within a few days as demonstrated by ^{1}H- and ^{31}P-NMR spectroscopy.

Spectroscopic Characterization of 3–5

The stereochemistry around the metal centers of the trimeric complexes **3**–**5** is reflected in their ^{1}H-, ^{13}C-, ^{31}P-NMR, and IR spectra, which are consistent with a C_3 symmetry in the molecules (Table 1). In the hydride region of the ^{1}H-NMR spectra of **3**–**5** each signal gives rise to triplet patterns caused by the interaction with two magnetically equivalent phosphorus nuclei. The magnitude of the coupling constants is typical of hydrides which are coordinated *cis* to phosphane ligands[19]. In the case of **4** the mutual coupling of the hydrides splits the triplets further into doublets. The interaction between the *cis* and *trans* hydrides in **5** results in additional splitting of the triplets into triplets and doublets, respectively. The chemical shifts of the hydrides reveal the *trans* influence of the ligands coordinated *trans* to them. According to the decreasing *trans* influence of the ligands in the order of H > CO > P ≫ Cl the shielding of the hydrides increases (Table 1)[20].

In contrast to the ^{31}P resonances of **2**–**5** which experience a coordination chemical shift of up to δ 43.4, the chemical shifts of the ^{13}C signals are hardly affected upon coordination of the tdppmcy ligand (**1**) to iridium (Table 1). In the alkane region of the ^{13}C{^{1}H}-NMR spectra of **3**–**5** three peaks are displayed in addition to the carbonyl resonances between δ 159 and 181 (Table 1). The signals of the carbonyl and ring methylene groups are observed as binominal triplets due to the coupling to two chemically equivalent phosphorus nuclei. While the methine signals ap-

Table 1. Selected ^{1}H-, ^{13}C-, ^{31}P-NMR, and IR data of **1**−**5**

Compound	^{1}H [δ][a]	^{13}C{^{1}H} [δ][a]				^{31}P{^{1}H} [δ][a]	IR (KBr) [cm^{-1}]
	Hydride	CH	CH$_2$	CH$_2$P	CO		ν(CO) / ν(MH)
1		34.8 (d) $^2J_{PC}$ = 13.8	42.8 (t) $^3J_{PC}$ = 9.7	36.4 (d) $^1J_{PC}$ = 12.7		-21.7 (s)	
2		36.2 (s)	43.1 (s)	33.9 (m) J = 16.4[b]	175.6 (br. s)	21.7 (s)	1957 /
3	-23.5 (t) 14.8[c]	34.6 (s)	42.5 (t) $^3J_{PC}$ = 8.4	40.2 (m) J = 18[b]	159.7 (t) $^2J_{PC}$ = 7.9	-16.6 (s)	2052 / 2259
4[d]	-8.2 (dt), -18.8 (dt) 19.2[c], 12.4[c], 4.8[e]	34.6 (s)	41.6 (t) $^3J_{PC}$ = 6.9	34.9 (br. s)	177.7 (br. s)	2.9 (s)	2081 / 1984 2200
5	-10.2 (dt), -11.1 (tt) 16.4[c], 20.9[c], 4.5[e]	36.7 (s)	40.8 (t) $^3J_{PC}$ = 3.6	41.8 (m) J = 37.8[b]	180.7 (t) $^2J_{PC}$ = 6.2	4.5 (s)	1959 / 2078 1772

[a] In CH_2Cl_2, CD_2Cl_2, respectively, except **5** in C_6D_6, coupling constants in Hz. − [b] A part of an AXX′ multiplet, $J = |^1J_{PC} + {}^3J_{PC}|$. − [c] $^2J_{PH}$. − [d] Preferentially formed diastereomer. − [e] $^2J_{HH}$.

pear as singlets, the interaction of the CH_2P groups with two phosphorus atoms along one and three bonds, respectively, generates the A part of an AXX′ pattern[11].

The ^{31}P{^{1}H}-NMR spectra of **3**−**5** show singlets in agreement with the C_3 symmetry of the trimeric metal complexes. These are shifted to higher field compared to the starting material **2** (Table 1). The ^{31}P{^{1}H}-NMR spectrum of the mixture of diastereomers **4** consists of four singlets in a 4:1:1:1 ratio.

The change from Ir(I) (**2**) to Ir(III) is illustrated by the shift of ν(CO) to higher energy in the IR spectra of **3**−**5** (Table 1)[21]. The absorptions of the IrH vibrations at 2259 and 2200 cm^{-1} in the IR spectra of **3** and **4**, respectively, are typical of H coordinated *trans* to Cl[22]. In contrast to the IrH vibration of H *trans* to CO in the IR spectrum of **4** at 1984 cm^{-1}, the corresponding IrD absorption has not been observed. In the IR spectrum of **4[D$_6$]** (which is obtained from **2** and D_2) ν(CO) is shifted by 53 cm^{-1} to lower frequency. This shift represents the resonance interaction of the vibrational states of ν(IrH) and ν(CO) and manifests the mutual *trans* positions of the hydrogen and carbonyl ligands[23].

In the IR spectrum of **5** intense absorptions are observed at 1772, 2078, and 1959 cm^{-1} which are caused by the mutual *trans* hydrides, the hydrogen *trans* to the carbonyl ligand and the CO ligand, respectively (Table 1)[17]. In the IR spectrum of **5[D$_9$]** (obtained by reducing **2** with $NaBD_4$) the absorption at 1772 cm^{-1} is replaced by one at 1271 cm^{-1} [ν(IrH)/ν(IrD) = 1.4]. The resonance interaction between the vibrational states of ν(IrH) and ν(CO) in the tris(hydridoiridium) complex **5** is analogous to that of the tris(dihydridoiridium) complex **4**. Because of the lower energy of ν(CO) compared to ν(IrH), the CO vibration is shifted to higher frequencies (35 cm^{-1})[23].

Conclusion

The influence of the cyclohexane ring on the coordination characteristics of tdppmcy is overruled by the chelate effect which promotes selective ring formation. Thus, either five-[7] or sixteen-membered rings but no unstable eight-membered chelates are formed[5]. This encourages the three diphenylphosphanyl groups of the tdppmcy ligand to bind to three different iridium atoms.

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Experimental

All manipulations were performed under pure argon by using Schlenk methods. All solvents were carefully dried and stored under argon. THF was freshly distilled from sodium/benzophenone prior to use. *cis,cis*-1,3,5-Tris[(diphenylphosphanyl)methyl]cyclohexane (**1**)[6] and $Ir(PPh_3)_2(CO)Cl$[24] were prepared according to literature procedures.

MS (FD): Finnigan MAT 711 A modified by AMD (8 kV, 60°C). − IR: Bruker IFS 48. − ^{31}P{^{1}H} NMR: Bruker AC 80 (32.44 MHz; ext. standard 1% H_3PO_4/[D$_6$]acetone). − ^{1}H and ^{13}C{^{1}H} NMR: Bruker AC 250 (250.13 and 62.90 MHz; ^{1}H chemical shifts were referenced to the residual proton peak of CH_2Cl_2 at δ 5.32 vs TMS. ^{13}C chemical shifts were referenced to CD_2Cl_2 at δ 53.8 vs TMS. In addition to the ^{13}C{^{1}H}-NMR spectrum a ^{13}C-DEPT[25] experiment was routinely recorded for each compound. The assignments of the resonances due to the protons in the ^{1}H-NMR spectra of compounds **2** and **5** were supported by two-dimensional homonuclear shift correlation (H,H-COSY[25]) experiments. The numbers of hydrides bound to the metal centers in **3**−**5** are confirmed on the basis of the multiplicities of the off-resonance proton-decoupled ^{31}P-NMR spectra. – Molecular mass: vapor pressure osmometer Fa. Knauer.

Tricarbonyl-1κC,2κC,3κC-trichloro-1κCl,2κCl,3κCl-bis{μ_3-cis,cis-1,3,5-tris[(diphenylphosphanyl)-1κP,2κP,3κP-methyl]cyclohexane}triiridium (**2**): A solution of 244 mg (0.36 mmol) of **1** and 420 mg (0.54 mmol) of $Ir(PPh_3)_2(CO)Cl$ in 30 ml of toluene was heated to 80°C for 3 h. After the reaction mixture had been reduced in volume to 10 ml, *n*-hexane (10 ml) was added and the pale yellow precipitate filtered, washed with toluene and pentane, and then dried under reduced pressure. Yield 320 mg (83%), m.p. >210°C (dec.). – ^{1}H NMR (CD_2Cl_2): $\delta = 0.59$ (dt, $^2J_{HH} = 11.1$, $^3J_{HH} = 11.8$ Hz, 6H, CH_aH_e), 2.07 (br. d, $^2J_{HH} = 11.1$ Hz, 6H, CH_aH_e), 2.2 (br. m, 6H, CH_2P), 2.6 (br. m, 6H, $CHCH_2P$), 2.8 (br. m, 6H, CH_2P), 7.1–7.8 (m, 60H, C_6H_5). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta =$ 131.0–135.5 (m, C_6H_5). – MS (FD), *m/z*: 2124.3 [M^+], molecular mass determination: 1970 g/mol. – $C_{93}H_{90}Cl_3Ir_3O_3P_6$ (2124.6): calcd. C 52.58, H 4.27, Cl 5.01; found C 52.35, H 4.36, Cl 5.29.

Tricarbonyl-1κC,2κC,3κC-trichloro-1κCl,2κCl,3κCl-trihydrido-1κH,2κH,3κH-bis{μ_3-cis,cis-1,3,5-tris[(diphenylphosphanyl)-1κP,2κP,3κP-methyl]cyclohexane}triiridium(3+)-tris(trifluoromethanesulfonate) (**3**): To a solution of 208 mg (0.1 mmol) of **2** in 10 ml of dichloromethane 26 µl (0.3 mmol) of trifluoromethanesulfonic acid was added at room temp. After stirring for 3 h the volume of the solution was reduced to 3 ml, and *n*-hexane was added. The precipitate was filtered, washed with pentane, and dried under reduced pressure. Yield 220 mg (87%), m.p. 176.8°C (dec.). – ^{1}H NMR (CD_2Cl_2): $\delta = -0.06$ (br. m, 6H, CH_aH_e), 1.78 (br. d, $^2J_{HH} = 11.1$ Hz, 6H, CH_aH_e), 2.1–2.3 (br. m, 18H, $CHCH_2P$), 7.2–7.7 (m, 60H, C_6H_5). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 118.9$ (q, $^1J_{FC} = 319.9$ Hz, CF_3), 125.0–135.6 (m, C_6H_5). – $C_{96}H_{93}Cl_3F_9Ir_3O_{12}P_6S_3$ (2574.8): calcd. C 44.78, H 3.64, Cl 4.13, F 6.64, S 3.74; found C 44.12, H 3.54, Cl 4.09, F 7.02, S 3.80.

Tricarbonyl-1κC,2κC,3κC-trichloro-1κCl,2κCl,3κCl-hexahydrido-1κ^2H,2κ^2H,3κ^2H-bis{μ_3-cis,cis-1,3,5-tris[(diphenylphosphanyl)-1κP,2κP,3κP-methyl]cyclohexane}triiridium (**4**): H_2 gas (D_2 gas) was passed through an intense yellow solution of **2** (100 mg, 0.05 mmol) in dichloromethane (30 ml) until the reaction mixture was discolored (ca. 2 h). After removal of the solvent under reduced pressure at room temp. **4** was isolated in quantitative yield. – IR (KBr, cm^{-1}): 2028 ν(CO) of **4-[D$_6$]**. – ^{1}H NMR (CD_2Cl_2): $\delta = -0.05$ (dt, $^2J_{HH} = 11.9$, $^3J_{HH} = 11.9$ Hz, 6H, CH_aH_e), 1.15 (br. d, $^2J_{HH} = 11.9$ Hz, 6H, CH_aH_e), 1.50 (m, 6H, CH_2P), 2.09 (br. m, 6H, $CHCH_2P$), 2.51 (m, 6H, CH_2P), 7.2–7.9 (m, 60H, C_6H_5). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta =$ 129.0–142.3 (m, C_6H_5). – $C_{93}H_{96}Cl_3Ir_3O_3P_6$ (2130.6): calcd. C 52.43, H 4.54, Cl 4.99; found C 52.75, H 4.62, Cl 5.01.

Tricarbonyl-1κC,2κC,3κC-nonahydrido-1κ^3H,2κ^3H,3κ^3H-bis{μ_3-cis,cis-1,3,5-tris[(diphenylphosphanyl)-1κP,2κP,3κP-methyl]-cyclohexane}triiridium (**5**): To a suspension of 50 mg (1.3 mmol) of $NaBH_4$ ($NaBD_4$) in 20 ml of THF was added dropwise a suspension of 100 mg (0.05 mmol) of **2** in 15 ml of THF. After stirring for 2 h the reaction mixture was separated from NaCl and residual $NaBH_4$, hydrolyzed, and dried with silica gel. Removal of the solvent and recrystallization of the residue from toluene/hexane gave 73 mg (77%) of colorless **5**; m.p. >160°C (dec.). – IR (KBr, cm^{-1}): 1994 ν(CO), 1271 ν(IrD) of **5[D$_9$]**. – ^{1}H NMR (C_6D_6): $\delta = -0.08$ (dt, $^2J_{HH} = 11.6$, $^3J_{HH} = 12.0$ Hz, 6H, CH_aH_e), 1.93 (br. d, $^2J_{HH} = 11.6$ Hz, 6H, CH_aH_e), 2.26 (br. s, 6H, CH_2P), 2.83 (m, 6H, $CHCH_2P$), 6.93–7.8 (m, 60H, C_6H_5). – $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta =$ 129.0–141.2 (m, C_6H_5). – $C_{93}H_{99}Ir_3O_3P_6$ (2027.3): calcd. C 55.1, H 4.92; found C 55.3, H 4.93.

☆ Dedicated to Professor *Reinhard Schmutzler* on the occasion of his 60th birthday.

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