Synthesis and Complexation Behavior of the Functionalized Tripodal Phosphane *cis,cis*-1,3,5-Tris(cyano)-1,3,5-tris(diphenylphosphanyl)-cyclohexane (tdppcycn)☆

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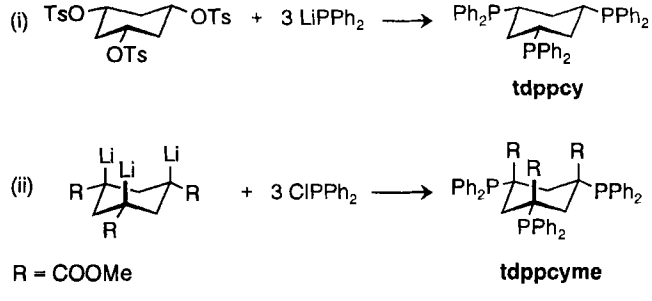
The synthesis of the novel potentially bistripodal ligand *cis-cis*-1,3,5-tris(cyano)-1,3,5-tris(diphenylphosphanyl)cyclohexane (tdppcycn) (**6**) is described. Starting from the tricarboxylic acid *cis,cis*-1,3,5-$C_6H_9(COOH)_3$ (**1**), which is converted stepwise into the triacid chloride *cis,cis*-1,3,5-$C_6H_9(COCl)_3$ (**2**), the triphenyl ester *cis,cis*-1,3,5-$C_6H_9(COOPh)_3$ (**3**), the tricarboxamide *cis,cis*-1,3,5-$C_6H_9(CONH_2)_3$ (**4**), and the tricarbonitrile *cis,cis*-1,3,5-$C_6H_9(CN)_3$ (**5**), we obtained tdppcycn (**6**) by α-deprotonation of **5** followed by treatment with $ClPPh_2$ in good yield. Treatment of **6** with $Mo(CO)_3(\eta^6\text{-}C_7H_8)$ and $Ir(PPh_3)_2(CO)Cl$ gave octahedral Mo(tdppcycn)$(CO)_3$ (**7**) and pentacoordinate Ir(tdppcycn)(CO)Cl (**8**), respectively, with a *facially* P-coordinated tdppcycn ligand. The stereochemistry of compounds **2**–**8** was established by ^1H-, ^{13}C-, ^{31}P-NMR, and IR spectroscopy. An X-ray crystal structure analysis of complex **8** confirms the trigonal-bipyramidal ground-state structure in the solid state.

The properties of polyphosphane ligands can be altered to control the stereochemistry of transition-metal complexes and thus to favor different kinds of reactions[2–5]. While the connectivities of the backbone of the polydentate phosphanes have been varied over a broad range, functionalization of the polyphosphanes has been less attractive[3,5,6]. Among the well established synthetic procedures to obtain phosphane ligands with novel structural features there are two routes which are widely applied[7]: (i) the reaction of metalated phosphanes with organic substrates which contain suitable leaving groups and (ii) the reaction of halogenophosphanes with organometallic reagents. Both methods have been employed in the synthesis of tripodal phosphanes with cyclohexane as a backbone (Scheme 1)[8,9]. The difficulty in controlling the stereochemistry of the nucleophilic substitution at the ring carbon atom according to method (i) leads to *cis,trans* isomerization and thus to poor yield[8]. In contrast, stabilization of the carbanions by adjacent electron-withdrawing groups in method (ii) allows a better control of the stereochemistry and results in high yield[9]. The introduction of functional groups into the *ipso* positions of the cyclohexane ring not only improves the synthesis of these phosphane ligands, but they also offer the opportunity to control the solubility, and may be used as spacers to support the metal complexes. In this paper we report the synthesis of a new functionalized phosphane ligand and the influence of the functional groups on the stability of the resulting metal complexes.

Scheme 1



Ligand Synthesis

The new tripodal phosphane ligand **6** was prepared by a five-step synthesis in an overall yield of 56% (Scheme 2). As starting material for the preparation of the key intermediate **5**, commercially available *cis,cis*-1,3,5-cyclohexanetricarboxylic acid (**1**) was chosen. The tricarboxylic acid **1** can be easily converted into the corresponding acid chloride **2** by treatment with an excess of $SOCl_2$ and a catalytic amount of DMF. The synthesis of **2** has been described previously, but no spectroscopic data have been reported[10]. Treatment of **2** with phenol in a dichloromethane/pyridine mixture afforded the phenyl ester of the *cis,cis*-1,3,5-cyclohexanetricarboxylic acid (**3**) which was converted into the corresponding tricarboxamide **4** by stirring a suspension of **3** in liquid ammonia. In contrast to earlier reports[11], the direct synthesis of the tricarboxamide **4** by treatment of the acid chloride **2** with gaseous ammonia or ammonium salts in solution gave hardly any monomeric **4**. Dehydration of the tricarboxamide **4** with $SOCl_2$ in DMF yielded the tricarbonitrile **5**, which was isolated after recrystallization from ethanol as colorless needles. According to method (ii) (Scheme 1) the new tripodal ligand *cis,cis*-1,3,5-tris(cyano)-

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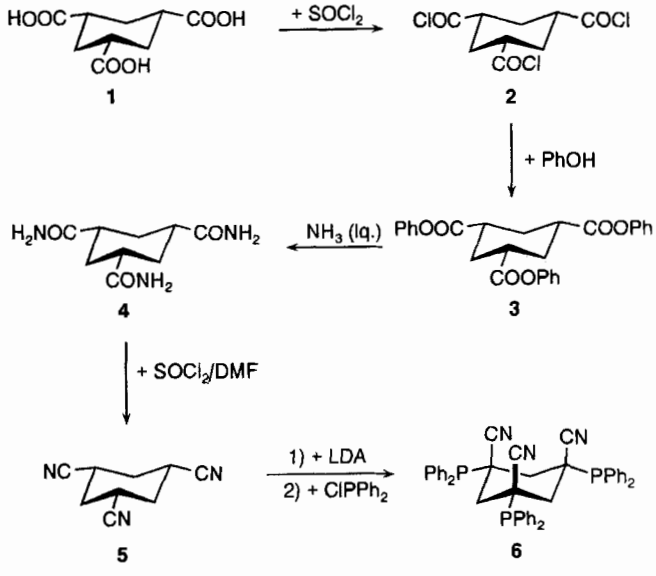
1,3,5-tris(diphenylphosphanyl)cyclohexane (tdppcycn) (**6**) was obtained by α-deprotonation of the tricarbonitrile **5** with lithium diisopropylamide and subsequent treatment with chlorodiphenylphosphane (Scheme 2). Since the stability of the in situ generated organotrilithium compound of the tricarbonitrile is strongly reduced compared to the corresponding trilithium compound of the triester, the reaction has to be performed at lower temperatures (−60 °C)[9,12]. The thermally stable colorless phosphane dissolves well in polar organic solvents.

Scheme 2

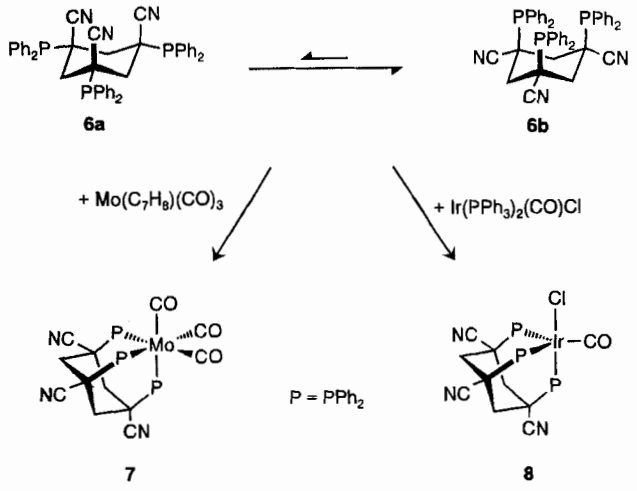


The *cis,cis* arrangement of the functional groups in **2**–**6** was established by ^{1}H- and ^{13}C-NMR spectroscopy. The alkane regions of the ^{1}H-NMR spectra of **2**–**5** display a doublet of triplets, a broad doublet and a triplet of triplets due to the axial and equatorial methylene protons and to the methine hydrogen atoms, respectively. The $^{13}C\{^1H\}$-NMR spectra of **2**–**5** show three singlets caused by the methylene, methine, and the carbon atoms of the functional groups.

The nonequivalent ring methylene hydrogen atoms in the ^{1}H-NMR spectrum of **6** give rise to a doublet of triplets (δ = 1.89, $^2J_{HH}$ = 14.0, $^3J_{PH}$ = 7.3 Hz) and a broad doublet (δ = 2.20, $^2J_{HH}$ = 14.0, $^3J_{PH}$ < 5 Hz). In the $^{13}C\{^1H\}$-NMR spectrum of tdppcycn (**6**) three signals are observed which are split by the interaction with the phosphorus nuclei into a doublet of triplets (δ = 31.7, $^1J_{PC}$ = 30.0, $^3J_{PC}$ = 10.2 Hz, CP), a triplet (δ = 38.3, $^2J_{PC}$ = 26.1 Hz, CH_2) and a doublet (δ = 118.3, $^2J_{PC}$ = 3.0 Hz, CN), respectively. The C_3 symmetry of the ligand is also consistent with a singlet in the $^{31}P\{^1H\}$-NMR spectrum. As a special feature, a weak ν(CN) absorption is observed at 2223 cm^{-1} in the IR spectrum of **6**.

Compound **6** represents a potentially bistripodal ligand which contains three hard and three soft donort functions. In the conformation **6a** (Scheme 3), the hard cyano groups with their electron pairs are oriented parallel to the C_3 axis. This steric arrangement is unfavorable for coordination to a single metal atom[13]. In the conformation of **6b** (Scheme 3), the three soft phosphanyl donor groups point towards the C_3 axis and thus are capable of binding to a single metal center forming adamantane-type structures[8,9].

Scheme 3



Complexation

The cycloheptatriene ligand of $Mo(CO)_3(\eta^6\text{-}C_7H_8)$ is replaced completely when tdppcycn (**6**) is allowed to react with the molybdenumcarbonyl complex in hot toluene (Scheme 3). The octahedral complex $Mo(CO)_3$(tdppcycn) (**7**) precipitates from the reaction mixture as an off-white powder. The spectroscopic data are consistent with all three phosphanyl groups coordinated *facially* to the molybdenumtricarbonyl fragment. This is demonstrated by a coordination chemical shift ($\Delta\delta$ = 15.2) of the $^{31}P\{^1H\}$-NMR resonance of **7**. The $^{13}C\{^1H\}$-NMR signals of the cyano groups are affected verry little ($\Delta\delta$ = 2.2) upon coordination of the tdppcycn ligand. In the $^{13}C\{^1H\}$-NMR spectrum, the ring methylene and the quaternary carbon atoms display complex multiplet patterns caused by the interaction with the phosphorus nuclei. Due to the C_{3v} symmetry of the molybdenum complex only two multiplets are observed for the axial and equatorial hydrogen atoms in the ^{1}H-NMR spectrum. The C_{3v} symmetry is distorted in the solid state which is indicated by the splitting of the E mode in the IR spectrum (KBr). In addition the ν(CN) band is shifted by 6 cm^{-1} to higher energy compared to non-complexed tdppcycn.

When $Ir(PPh_3)_2(CO)Cl$ is treated with an equimolar amount of tdppcycn (**6**) in hot toluene according to the procedure of the Ir(tdppcy)(CO)Cl [tdppcy = *cis,cis*-1,3,5-tris(diphenylphosphanyl)cyclohexane] synthesis[8], the color of the solution changes from yellow to orange. An equilibrium between Vaska's compound and tdppcycn, and **8** and PPh_3 is formed:

$$Ir(PPh_3)_2(CO)Cl + tdppcycn \rightleftharpoons [Ir(tdppcycn)(PPh_3)_n(CO)Cl] + (2-n)PPh_3 \quad (1)$$

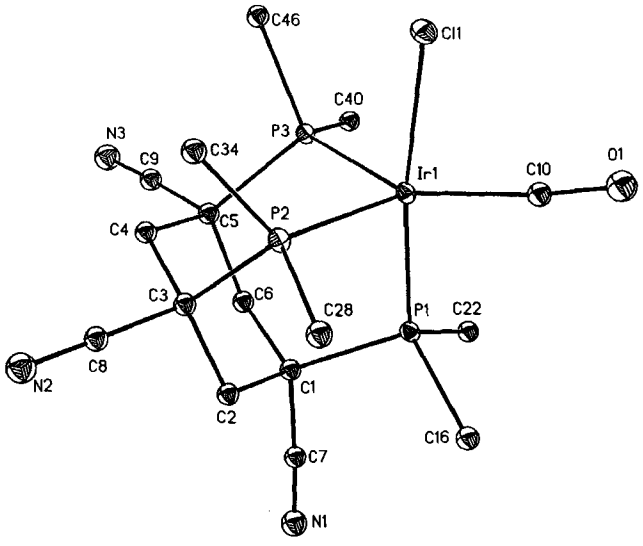
Precipitation with *n*-hexane results in $Ir(PPh_3)_2(CO)Cl$ as the major product and minor amounts of **8**. The equilibrium of equation 1 can be shifted to the right by continuous removal of the triphenylphosphane. This was performed in a liquid-liquid extractor with *n*-hexane as the extracting solvent and DMSO as the reaction medium. This technique allows the isolation of the orange complex **8** in high yield (Scheme 3). If PPh_3 is added to a solution of **8** in hot toluene Vaska's compound and tdppcycn (**6**) is formed according to equation 1. The $^{31}P\{^1H\}$-NMR spectrum of the reaction mixture displays a singlet for the free ligand and for the complex **8** and a broad resonance due to free PPh_3. In contrast to Ir(tdppcy)(CO)Cl which decomposes in solution and in the solid state[8], Ir(tdppcycn)(CO)Cl (**8**) is stable under both conditions. The introduction of the cyano groups into the backbone of the ligand also improves the solubility of the metal complex **8**.

Upon coordination of tdppcycn (**6**) to the Ir(CO)Cl fragment the ^{31}P resonance is shifted to higher field ($\delta = -3.5$). The singlet which is observed at room temperature is in agreement with a highly fluxional pentacoordinate iridium complex. When the temperature is lowered the signal remains sharp until below −70 °C the line shape gradually broadens. Cooling to −102 °C results in further broadening of the line shape; however, a decoalescence is not observed. Thus, the barrier to pseudo rotation in **8** is lower than that found in Ir(tdppcy)(CO)Cl and in other related pentacoordinate complexes of the type M(tdpme)(CO)X (M = Rh, Ir; X = Cl, H, alkyl) with the tripodal phosphane ligand $MeC(CH_2PPh_2)_3$ (tdpme)[8,14–17]. The low energy exchange process in **8** prevents the distinction between a square pyramid and a trigonal bipyramid as the ground-state geometry of Ir(tdppcycn)(CO)Cl in solution. The high fluxionality in solution is also responsible for the observation of single multiplets for the methylene groups, the quaternary ring carbon atoms, and the cyano groups in the $^{13}C\{^1H\}$-NMR spectrum. Only two multiplets due to the equatorial and axial ring methylene hydrogen atoms are seen in the alkane region of the ^1H-NMR spectrum.

While the IR spectrum of a solution of **8** in $CHCl_3$ displays a single ν(CO) band at 1956 cm^{-1} the IR spectra taken in the solid state (KBr pellet) show up to two absorptions in the range of 1928–1951 cm^{-1}. This may be explained in terms of polymorphism which is also consistent with the observation of several peaks in the solid-state ^{31}P-CP/MAS NMR spectrum. Although all three phosphanyl groups are coordinated to the metal center, the carbonyl absorption appears at higher frequencies than those found for Ir(tdppcy)(CO)Cl (1899 cm^{-1})[8] and Ir(tdpme)(CO)Cl (1907 cm^{-1})[18]. This indicates that the electron donating ability of the functionalized tdppcycn ligand is strongly reduced compared to the tdppcy and tdpme phosphanes.

An ORTEP drawing of the single-crystal X-ray structure analysis of complex **8** which establishes the molecular constitution as deduced from NMR and IR spectroscopy is shown in Figure 1. The stereochemical constraints of the tdppcycn ligand imposes a trigonal-bipyramidal geometry around iridium. The three diphenylphosphanyl groups are facially coordinated occupying two equatorial and one apical position. Due to its better π-acceptor ability the CO prefers the equatorial position while the chlorine atom is axially oriented[19]. The angle between the equatorial phosphanyl groups P2–Ir–P3 is strongly reduced (95.9°) compared to 120° of the ideal geometry but is significantly larger than in the complexes Ir(tdpme)(CO)Cl (90.3°)[15] and Rh(tdpme)(CO)Me (90.8°)[17]. As a consequence, the P3–Ir–C10 and P2–Ir–C10 angles are opened to 135.8° and 127.7°, respectively. The overall sum of 359.4° shows that the equatorial plane is not distorted. As in Ir(tdpme)(CO)Cl and Rh(tdpme)(CO)Me, the $P_{equatorial}$–metal distances are longer than the P_{axial}–metal distance. The cyclohexane ring deviates from the ideal chair conformation and C_3 symmetry which is expressed in different endocyclic bond and ring torsional angles (Fig. 1). The widening of the endocyclic bond angles between the CH_2 groups to 116.2° (average value) compared to 111.5° in cyclohexane[20] leads to a change in the torsional angles of up to 49° (55° in cyclohexane[20]) and to a flattening of the cyclohexane ring.

Figure 1. ORTEP plot of Ir(tdppcycn)(CO)Cl (**8**); only the *ipso* carbon atoms of the phenyl rings are shown for clarity[a]



[a] Selected bond distances [pm]: Ir–C(10) 188.0(5), Ir–P(1) 226.7(2), Ir–P(3) 235.2(2), Ir–P(2) 235.3(2), Ir–Cl 242.9(2), O–C(10) 113.3(6); bond angles [°]: C(10)–Ir–P(3) 135.8(2), C(10)–Ir–P(2) 127.7(2), P(1)–Ir–P(3) 91.82(5), P(1)–Ir–P(2) 95.27(5), P(3)–Ir–P(2) 95.89(4), C(10)–Ir–Cl 81.4(2), P(1)–Ir–Cl 172.63(4), C(3)–C(2)–C(1) 115.7(4), C(5)–C(4)–C(3) 117.0(4), C(5)–C(6)–C(1) 115.9(4); torsional angles [°]: C(1)–C(2)–C(3)–C(4) 46.6(5), C(2)–C(3)–C(4)–C(5) −45.8(5), C(3)–C(4)–C(5)–C(6) 47.0(6), C(4)–C(5)–C(6)–C(1) −50.5(4), C(2)–C(1)–C(6)–C(5) 52.1(5), C(6)–C(1)–C(2)–C(3) −49.8(5).

Conclusion

The functionalization of the cyclohexane ring with electron-withdrawing cyano groups leads to the new potentially bistripodal ligand **6**. For both steric and electronic reasons **6** coordinates exclusively via the three phosphanyl groups *facially* to the $Mo(CO)_3$ and Ir(CO)Cl fragments. The cyano groups considerably reduce the electron density on the metal centers which might be the origin of the increased

stability of the pentacoordinated Ir(tdppcycn)(CO)Cl complex compared to Ir(tdppcy)(CO)Cl. A further benefit of the functional groups is the better solubility of the metal complexes.

We thank Professor *E. Lindner* for his support and the *Degussa AG* for providing $IrCl_3 \cdot xH_2O$.

Experimental

All manipulations were performed under pure argon by using Schlenk methods. All solvents were carefully dried. Diethyl ether, THF, and toluene were freshly distilled from sodium/benzophenone, DMSO, pyridine, diisopropylamine, chloroform, and dichloromethane from CaH_2, DMF from CaO, and *n*-pentane and *n*-hexane from $LiAlH_4$ prior to use. *cis,cis*-1,3,5-Cyclohexanetricarboxylic acid was purchased from Aldrich. $Mo(CO)_3(\eta^6\text{-}C_7H_8)$[21] and $Ir(PPh_3)_2(CO)Cl$[22] were prepared according to literature procedures.

MS (FD): Finnigan MAT 711 A modified by AMD (8 kV, 60°C). – IR: Bruker IFS 48. – $^{31}P\{^1H\}$ NMR: Bruker AC 80 (32.44 MHz; ext. standard 1% H_3PO_4/[D_6]acetone); variable temperature experiments: Bruker AMX400 (161.98 MHz): – ^1H and $^{13}C\{^1H\}$ NMR: Bruker AC 250 (250.13 and 62.90 MHz; ^1H chemicals shifts were referenced to the residual proton peak of CH_2Cl_2 at $\delta = 5.32$ vs TMS. ^{13}C chemical shifts were referenced to CD_2Cl_2 at $\delta = 53.8$ vs TMS. In addition to the $^{13}C\{^1H\}$-NMR spectrum a ^{13}C-DEPT[23] experiment was routinely performed for each compound. – ^{31}P CP/MAS: Bruker ASX300 (121 MHz). – Single-crystal X-ray structure determination of **8**: Siemens P4 diffractometer. – Elemental analysis: Carlo Erba 1106.

cis,cis-1,3,5-Cyclohexanetricarbonyl Trichloride (**2**): A mixture of 21.62 g (100 mmol) of finely grounded **1**, 32.82 ml (450 mmol) of freshly distilled $SOCl_2$, and one drop of DMF was slowly heated to 80°C. After completion of the gas generation the temperature was raised to 90°C and the mixture was maintained at this temp. for an additional 2 h. Removal of excess $SOCl_2$ and traces of HCl and SO_2 under reduced pressure for 5 h at 50°C yielded **2** as a colorless oil, which solidified on standing. Yield 27.15 g (100%), m.p. 46°C. – IR (KBr, cm^{-1}): 1796 ν(CO). – ^1H NMR (CD_2Cl_2): $\delta = 1.69$ (dt, $^2J_{HH} = 11.2$, $^3J_{HH} = 12.7$ Hz, 3H, CH_aH_e), 2.68 (br. d, $^2J_{HH} = 11.2$, $^3J_{HH} = 3.4$ Hz, 3H, CH_aH_e), 2.92 (tt, $^3J_{HH} = 12.7$, $^3J_{HH} = 3.4$ Hz, 3H, CH). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 30.6$ (s, CH_2), 52.5 (s, CH), 174.9 (s, COCl). – MS (FD), *m/z*: 270.0 [M^+]. – $C_9H_9Cl_3O_3$ (271.5): calcd. C 39.81, H 3.34, Cl 39.17; found C 39.96, H 3.34, Cl 39.20.

Triphenyl-cis,cis-1,3,5-cyclohexanetricarboxylate (**3**): A solution of 42.35 g (450 mmol) of phenol in 100 ml of pyridine was added dropwise to a solution of 27.15 g (100 mmol) of **2** in 150 ml of dichloromethane cooled to 0°C over a period of 1 h. After the resulting orange-colored suspension had been heated at 40°C for 12 h, it was washed twice with 150 ml of water each, 150 ml of 0.1 N HCl each, 150 ml of water each, and once with 100 ml of brine. Drying of the organic layer with $CaCl_2$ and removal of the solvent under reduced pressure gave **3** as a yellow oil, which solidified on standing. Recrystallization of the crude product from chloroform/diethyl ether (40 ml/20 ml) yielded **3** as fine white needles. Yield 37.16 g (83%), m.p. 130°C. – IR (KBr, cm^{-1}): 1745 ν(CO). – ^1H NMR (CD_2Cl_2): $\delta = 1.82$ (dt, $^2J_{HH} = 12.8$, $^3J_{HH} = 12.6$ Hz, 3H, CH_aH_e), 2.58 (br. d, $^2J_{HH} = 12.8$, $^3J_{HH} = 3.3$ Hz, 3H, CH_aH_e), 2.72 (tt, $^3J_{HH} = 12.6$, $^3J_{HH} = 3.3$ Hz, 3H, CH), 7.00–7.34 (m, 15H, C_6H_5). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 30.4$ (s, CH_2), 42.0 (s, CH), 121.1 (s, *ortho*-C_6H_5), 126.0 (s, *para*-C_6H_5), 129.5 (s, *meta*-C_6H_5), 150.6 (s, *ipso*-C_6H_5), 172.3 (s, COO). – MS (FD), *m/z*: 445.3 [$M^+ + H$], 351.2 [$M^+ - OC_6H_5$]. – $C_{27}H_{24}O_6$ (444.5): calcd. C 72.96, H 5.44; found C 72.45, H 5.41.

cis,cis-1,3,5-Cyclohexanetricarboxamide (**4**): 22.22 g (50 mmol) of **3** was suspended in 300 ml of liquid NH_3 at −40°C. After the off-white suspension had been vigorously stirred for 15 h, NH_3 was evaporated. The remaining off-white solid was carefully washed three times with 200 ml of diethyl ether each, three times with 200 ml of dichloromethane each, and then dried under reduced pressure. Yield 10.48 g (98%), m.p. 290°C (dec.). – IR (KBr, cm^{-1}): 3345, 3192 ν(NH), 1675 ν(CO) amid I, 1625 ν(NCO) + δ(NH) amid II. – ^1H NMR (DCl): $\delta = 1.73$ (dt, $^2J_{HH} = 12.3$, $^3J_{HH} = 12.4$ Hz, 3H, CH_aH_e), 2.43 (br. d, $^2J_{HH} = 12.3$, $^3J_{HH} = 3.1$ Hz, 3H, CH_aH_e), 3.05 (tt, $^3J_{HH} = 12.4$, $^3J_{HH} = 3.1$ Hz, 3H, CH). – $^{13}C\{^1H\}$ NMR (DCl): $\delta = 30.3$ (s, CH_2), 41.3 (s, CH), 181.4 (s, $CONH_2$). – MS (IS), *m/z*: 213.5 [M^+]. – $C_9H_{15}N_3O_3$ (213.2): calcd. C 50.70, H 7.09, N 19.71; found C 50.62, H 7.14, N 20.10.

cis,cis-1,3,5-Cyclohexanetricarbonitrile (**5**): 21.88 ml (300 mmol) of freshly distilled $SOCl_2$ was added dropwise to a suspension of 10.66 g (50 mmol) of **4** in 250 ml of DMF at room temp. After heating of the resulting red-brown solution at 45°C for 15 h, the solution was allowed to cool to room temp. It was then poured on a mixture of 150 g of crushed ice and 60 g of Na_2CO_3 and the mixture was stirred until CO_2 evolution was finished. The hydrolysis mixture was then extracted three times with 200 ml of dichloromethane each. The combined organic phases were dried with $CaCl_2$. The solvent was removed under reduced pressure until a red-brown tough, partially crystallizing oil remained. The oil was dissolved in 250 ml of boiling ethanol and the solution was decolorized with activated carbon. The boiling solution was concentrated until it became cloudy. Upon standing at room temp. long colorless needles of **5** formed. Further crops of crystals could be obtained from the mother liquor. Yield 6.10 g (76%), m.p. 175°C. – IR (KBr, cm^{-1}): 2251 ν(CN). – ^1H NMR (CD_2Cl_2): $\delta = 1.68$ (dt, $^2J_{HH} = 12.6$, $^3J_{HH} = 12.6$ Hz, 3H, CH_aH_e), 2.30 (br. d, $^2J_{HH} = 12.6$, $^3J_{HH} = 3.5$ Hz, 3H, CH_aH_e), 2.40 (tt, $^3J_{HH} = 12.6$, $^3J_{HH} = 3.5$ Hz, 3H, CH). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 26.6$ (s, CH_2), 31.4 (s, CH), 119.2 (s, CN). – MS (FD), *m/z*: 160.1 [$M^+ + H$]. – $C_9H_9N_3$ (159.2): calcd. C 67.91, H 5.70, N 26.40; found C 68.42, H 5.72, N 26.30.

cis,cis-1,3,5-Tris(cyano)-1,3,5-tris(diphenylphosphanyl)cyclohexanetricarbonitrile (**6**): A solution of 0.85 ml (6.0 mmol) of diisopropylamine in 50 ml of diethyl ether, which was cooled to −60°C, was treated with 3.75 ml of a 1.6 M solution of *n*-BuLi/*n*-hexane during 15 min. The off-white solution was stirred for 10 min and a solution of 318.4 mg (2.0 mmol) of **5** in a mixture of 60 ml THF and 30 ml diethyl ether cooled to −60°C was added dropwise over a period of 30 min. After the off-white suspension had been stirred for an additional 10 min, a solution of 1.10 ml (6.0 mmol) of chlorodiphenylphosphane in 60 ml of diethyl ether kept at −60°C was added dropwise over a period of 20 min. The stirred suspension was allowed to warm to room temp. for 12 h. Upon standing a fluffy off-white precipitate sedimented from the reaction mixture. The solvent was decanted and to the remaining vigorously stirred mixture 75 ml of degassed HCl (75 ml of H_2O/0.2 ml of HCl 32%) was added. The white precipitate was filtered, washed three times with 25 ml of degassed water each, twice with 10 ml of diethyl ether each and dried in vacuo. Yield 1.20 g (84%), m.p. 283°C (dec.). – IR (KBr, cm^{-1}): 2223 ν(CN). – $^{31}P\{^1H\}$ NMR ($CHCl_3$): $\delta = 20.4$ (s). – ^1H NMR ($CDCl_3$): $\delta = 1.89$ (dt, $^2J_{HH} = 14.0$, $^3J_{PH} = 7.3$ Hz, 3H, CH_aH_e), 2.20 (br. d, $^2J_{HH} = 14.0$, $^3J_{PH} < 5$ Hz, 3H, CH_aH_e), 7.30–7.60 (m, 15H, C_6H_5). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 31.7$ (dt, $^1J_{PC} = 30.0$, $^3J_{PC} = 10.2$ Hz, CP), 38.3 (t, $^2J_{PC} = 26.1$

Hz, CH_2), 118.3 (d, $^2J_{PC}$ = 3.0 Hz, CN), 128.9 (d, $^3J_{PC}$ = 9.1 Hz, *meta*-C_6H_5), 130.5 (d, $^1J_{PC}$ = 16.1 Hz, *ipso*-C_6H_5), 130.8 (s, *para*-C_6H_5), 134.4 (d, $^2J_{PC}$ = 22.1 Hz, *ortho*-C_6H_5). – MS (FD), *m/z*: 711.4 [M^+]. – $C_{45}H_{36}N_3P_3$ (711.7): calcd. C 75.94, H 5.10, N 5.90; found C 75.51, H 5.17, N 6.23.

Tricarbonyl[cis,cis-1,3,5-tris(cyano)-1,3,5-tris(diphenylphosphanyl)cyclohexane]molybdenium (**7**): A suspension of 54.4 mg (0.2 mmol) of $Mo(CO)_3(\eta^6\text{-}C_7H_8)$ and 142.3 mg (0.2 mmol) of **6** in 10 ml toluene was heated at 80°C for 2 h during which time an off-white precipitate formed. This was collected on a sintered glass frit, washed twice with 1 ml of toluene each, three times with 10 ml of *n*-pentane each, and dried in vacuo. Yield 159.1 mg (89%), m.p. 322°C (dec.). – IR (KBr, cm^{-1}): 2229 ν(CN), 1961, 1881, 1864 ν(CO). – $^{31}P\{^1H\}$ NMR (pyridine): δ = 35.6 (s). – ^1H NMR ([D_5]pyridine): δ = 2.91–2.95 (m, 3H, CH_aH_e), 3.19–3.35 (m, 3H, CH_aH_e), 7.14–7.62 (m, 15H, C_6H_5). – $^{13}C\{^1H\}$ NMR ([D_5]pyridine): δ = 33.8 (s, CH_2), 34.6 (br. m, CP), 120.5 (s, CN), 128.7 (br. s, *meta*-C_6H_5), 130.9 (s, *para*-C_6H_5), 134.7–134.8 (m, *ortho*-C_6H_5), 135.0 (br. m, *ipso*-C_6H_5), 217.9–218.1 (m, CO). – MS (FAB), *m/z*: 893.5 [M^+]. – $C_{48}H_{36}MoN_3O_3P_3$ (891.7): calcd. C 64.66, H 4.07, N 4.71; found C 64.54, H 4.24, N 4.61.

Carbonylchloro[cis,cis-1,3,5-tris(cyano)-1,3,5-tris(diphenylphosphanyl)cyclohexane]iridium (**8**): A solution of 712 mg (1.0 mmol) of **6** and 780 mg (1.0 mmol) of $Ir(PPh_3)_2(CO)Cl$ in 100 ml of DMSO was extracted with *n*-hexane for 4 h in a liquid-liquid extractor. DMSO was removed from the orange reaction mixture under reduced pressure. The remaining orange solid was dissolved in 20 ml of dichloromethane. On addition of 50 ml of *n*-pentane to this solution an orange precipitate formed, which was collected on a sintered glass frit, washed three times with 10 ml of *n*-pentane each, and dried in vacuo. Yield 889.0 mg (92%), m.p. 269°C (dec.). – IR (KBr, cm^{-1}): 2229 ν(CN), 1928–1951 ν(CO) number of peaks varies from one to two; ($CHCl_3$, cm^{-1}): 1956 ν(CO). – $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = −3.5 (s). – ^{31}P CP/MAS: δ = 0.5 to −15.0 (several singlets). – ^1H NMR (CD_2Cl_2): δ = 2.88–3.05 (m, 3H, CH_aH_e), 3.31–3.38 (m, 3H, CH_aH_e), 7.12–7.62 (m, 15H, C_6H_5). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 30.8–30.9 (m, CP), 36.7 (br. m, CH_2), 120.5 (br. s, CN), 128.6–128.7 (m, *meta*-C_6H_5), 131.4 (s, *para*-C_6H_5), 134.1–134.2 (m, *ortho*-C_6H_5), 130.5–131.0 (m, *ipso*-C_6H_5). – MS (FAB), *m/z*: 966.9 [M^+]. – $C_{46}H_{36}ClIrN_3OP_3$ (967.4): calcd. C 57.11, H 3.75, N 4.34, Cl 3.67; found C 56.97, H 4.03, N 4.59, Cl 3.51.

X-Ray Structure Determination of **8**[24]: Single crystals (size 0.50 × 0.40 × 0.20 mm) were grown from chloroform/*n*-hexane. Siemens P4 diffractometer; graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å); formula $C_{46}H_{36}ClIrN_3OP_3 \cdot CHCl_3$; mol. mass 1086.71; space group $P2_1/c$ (No. 14); a = 12.984(4), b = 18.460(6), c = 18.637(5) Å, β = 107.92(1)°; F(000) 2152; V = 4250(2) Å^3; $\rho_{calcd.}$ = 1.698 g/cm^3; Z = 4; μ(Mo-K_α) = 3.548 mm^{-1}, 2Θ = 4–50°, ω scans; $-15 < h < 12$, $-21 < k < 21$, $-22 < l < 22$; 28384 reflections measured, unique reflexions 7498, 5056 considered observed [$I > 2\sigma(I)$]; 533 variables. The structure was solved by Patterson methods[25] and refined by least squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions (riding model). Maximum and minimum peaks in the final difference synthesis were 1.04 and −1.58 eÅ^{-3}. The R and wR_2 values were 0.0313 and 0.0810. The asymmetric unit contains one solvent molecule of $CHCl_3$.

☆ Dedicated to Prof. *William C. Kaska* on the occasion of his 60th birthday.

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