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Control of the basicity of the Ir(tdppcymome)(CO)Cl complex with methoxymethyl functional groups at the ligand backbone [tdppcymome = *cis,cis*-1,3,5-$(PPh_2)_3$-1,3,5-$(CH_2OCH_3)_3$-C_6H_6]

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Abstract

Treatment of the tripodal ligand *cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxymethyl)cyclohexane (tdppcymome) (**L**) with $Ir(PPh_3)_2(CO)Cl$ leads to the trigonal bipyramidal complex **4**. Ir(tdppcymome)(CO)Cl (**4**) is protonated by the strong and weak acid HBF_4 and NH_4PF_6, respectively. The oxidative addition of H_2 forces the chlorine to dissociate irreversibly from the metal center of **4**. In a CO atmosphere complex **4** forms the dicarbonyl complex $[Ir(tdppcymome)(CO)_2]Cl$ (**6**). The reaction of **4** with ethylene in the presence of $NaBPh_4$ gives the ethylene complex $[Ir(tdppcymome)(CO)(C_2H_4)]BPh_4$ (**8**). At elevated temperatures **8** looses ethylene under the formation of the orthometalated complex **9**. This complex can also be generated directly from **4** and $NaBPh_4$. EXAFS investigations on the carbonyl chlorocomplexes **1**–**4** display a remarkable change in the Ir–C bond length dependent on the functional group in the ligand backbone, while their ν(CO) absorptions correlate with the group electronegativity of the functional groups. © 1998 Elsevier Science S.A.

Keywords: EXAFS; Carbonyl chlorocomplexes; Tripodal phosphine; Iridium

1. Introduction

The popularity of tertiary polyphosphines as ligands is a result of their steric versatility which derives from the decisive variation of the substituents at phosphorus and the backbones [1–3]. Stoichiometric and catalytic conversions of substrate molecules can be controlled by a generation of a particular stereochemistry and electronic configuration at the metal center of polyphosphine complexes. The knowledge about the interplay between structure and reactivity of organometallic compounds led to the development of new catalytic processes in industry [4,5]. Tripodal phosphine ligands with three diphenylphosphine groups stereospecifically bound *cis,cis* to the 1,3,5 positions of the cyclohexane ring [6–8] control the stereochemistry by coordinating facially to transition metals like molybdenum, rhodium and iridium, thus generating a metal template {M(tripod)} of an adamantane-type polyhedron (Scheme 1). Moreover functional groups of different group electronegativity at the *ipso*-positions of the cyclohexane ring allow to modulate the electron density at the metal center. This has been demonstrated recently by the altered reactivity of the adamantane-type complexes Ir(tripod)(CO)Cl [tripod = *cis,cis*-1,3,5-tris-(diphenylphosphino)cyclohexane (tdppcy), *cis,cis*-1,3,5-tris-(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane(tdppcyme) *cis,cis*-1,3,5-tricyano-*cis,cis*-1,3,5-tris(diphenylphosphino)cyclohexane(tdppcycn)] **1**–**3** toward H^+, H_2, CO, and C_2H_4 [9].

Here we wish to outline a qualitative description of the influence of the functional groups on the metal electron density by means of a correlation of the group electronegativity and the ν(CO) absorption of a series of monocarbonyl iridium complexes. This correlation is in good agreement with the reactivity of the previously described compounds **1**–**3** and the new member Ir (tdppcymome)(CO)Cl (tdppcymome = *cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxymethyl)cycl-

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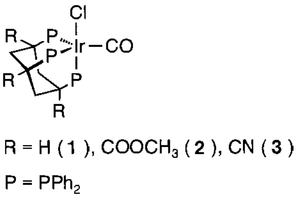


Scheme 1.

ohexane[10] (**4**) towards the above mentioned Broensted and Lewis acids. Furthermore structural information around the reactive center has been obtained by EXAFS investigations on compounds **1**–**4**.

2. Results and discussion

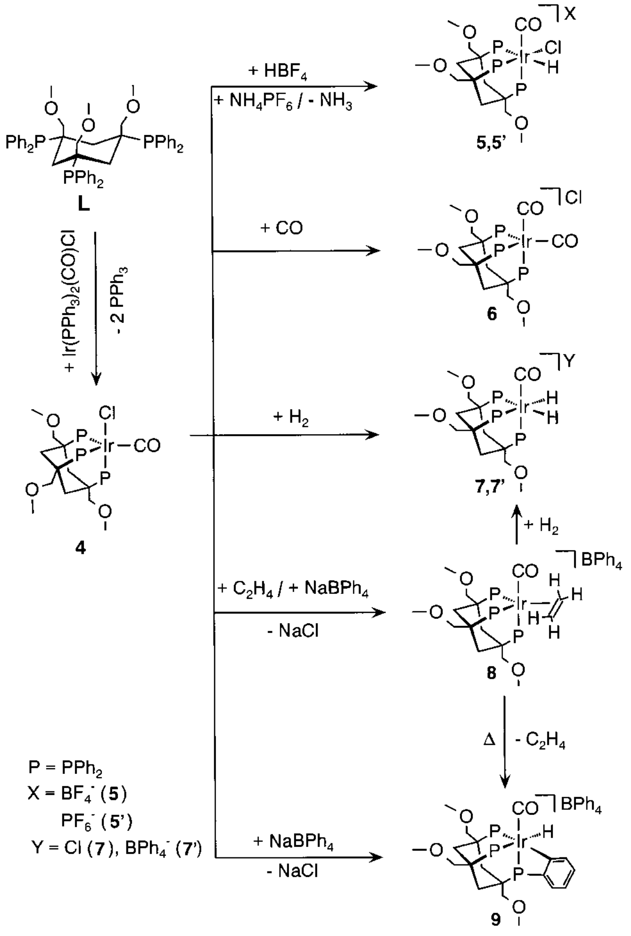
2.1. Synthesis and reactivity of Ir(tdppcymome)(CO)Cl (4)

When Ir(PPh$_3$)$_2$(CO)Cl is treated with an equimolar amount of the potentially tripodal phosphine ligand tdppcymome (**L**) in toluene at 80°C, an orange solution and little precipitate of the carbonyl chlorocomplex **4** is formed. ^{31}P{^{1}H} NMR and IR spectroscopic investigations of this solution lead to the conclusion, that an equilibrium between the tripodal ligand, the Vaska complex, triphenylphosphine and carbonylchlorophosphine species of the stoichiometry Ir($\eta^{n,n+1}$tdppcymome)(PPh$_3$)$_{2-n}$(CO)Cl ($n = 0$–2) exists. With increasing temperature the equilibrium is shifted towards Ir(tdppcymome)(CO)Cl (**4**) (Scheme 2). The precipitation of **4** is completed by slow addition of n-heptane to the reaction mixture at 80°C. Complex **4** decomposes in the solid state at room temperature during several days even when kept under an argon atmosphere. The compound is air-sensitive, especially in solution. Solutions of **4** in halogenated hydrocarbons are photolabile and decompose on exposure to daylight as seen by decolorization within a few hours. Several decomposition products could be detected by ^{31}P{^{1}H} NMR spectroscopy.

The strength of the basicity of the carbonylchloro complex **4** can be estimated from IR spectroscopy. The ν(CO) absorption at 1920 cm^{-1} suggests a basicity between complexes **1** and **2** [9]. This position is in agreement with the readily protonation of Ir(tdppcymome)(CO)Cl (**4**) by the strong acid HBF$_4$ as well as by the weak acid NH$_4$PF$_6$ (Scheme 2). Whereas the more basic complex **1** behaves similar, **2** and **3** are only protonated by the strong acid HBF$_4$ due to their lower metal electron density [6,9]. The octahedral cationic monohydrides **5**,**5′** (Scheme 2) are obtained as colorless to off-white powders which are less air-sensitive and dissolve readily in polar organic solvents.

A rapid and irreversible reaction of a solution of **4** in dichloromethane with the π-acid CO leads to the pentacoordinated cationic dicarbonyl complex **6**. When **4** is treated with H$_2$ in dichloromethane, the octahedral dihydride complex **7** is formed quantitatively (Scheme 2). The oxidative addition of H$_2$ forces the chlorine to dissociate from the metal center irreversibly. Addition of excess ethylene and NaBPh$_4$ to **4** in dichloromethane yields the cationic ethylene complex **8** within 10 h. The complexes **6**, **7**, and **8** can be isolated in high yields as pale yellow powders which are less air-sensitive than **4**. They are stable in the solid state and can be stored in an oxygen free atmosphere. [Ir(tdppcymome)(CO)(C$_2$H$_4$)]BPh$_4$ (**8**) reacts with hydrogen at normal pressure and room temperature slowly to the carbonyldihydrido complex **7′**. In the course of this oxidative addition ethylene is liberated, hydrogenation to ethane does not occur under these conditions.

When a solution of the ethene complex **8** in halogenated hydrocarbons is allowed to warm above 10°C complex **8** decomposes with loss of ethene. The formation of the orthometalated complex **9** is observed in the ^{31}P{^{1}H} NMR spectrum. The reaction can be completed



Scheme 2.

if the sample is warmed to room temperature in the presence of $NaBPh_4$. Anion exchange of the chlorine anion vs. the noncoordinating BPh_4^- in Ir(tdppcymome)(CO)Cl (**4**) generates a reactive angular d^8 ML_4 fragment [9,11] which successively leads to the formation of the cationic orthometalated carbonylhydrido complex **9** (Scheme 2). Complex **9** can be isolated in high yields as an off-white, air stable powder.

*2.2. Spectroscopic characterization (**4–9**)*

Owing to the relatively 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 spectrum of **4** (1920 cm^{-1}) is rather low. The ν(CO) absorptions in the complexes **5–9** are shifted to higher frequencies (1957–2083 cm^{-1}) due to a reduced electron density at the metal centers. The ν(Ir–H) of **5**, **7**, and **9** appear in the range of 2080–2161 cm^{-1}, and are typical for hydrogen *trans* to a strong *trans*-influence ligand [12].

The NMR spectra of the pentacoordinated d^8 carbonylchloro complex **4**, the dicarbonyl complex **6**, and the carbonylethene complex **8** illustrate a stereochemical nonrigid behavior. The $^{31}P\{^1H\}$ NMR spectra of **4** and **6** at room temperature display singlets at $\delta = 8.8$ and -2.3, respectively, which are consistent with a chemical exchange of the apical and equatorial phosphorus nuclei. When the temperature of a solution of **4** in dichloromethane is lowered the signal remains sharp until below -60°C the lineshape gradually broadens, indicating that the exchange process is slowed down. At the lowest accessible temperature of -100°C no coalescence can be observed. The *pseudo* C_{3v} symmetry of **4** and **6** is also coincident with the number of proton resonances in their ^1H NMR spectra. Only one signal for each functional group is shown, respectively. The methyl groups are characterized by a singlet, the protons of the exocyclic methylene groups give a broad singlet (**4**) and a doublet (**6**), respectively caused by the interaction with the phosphorus nuclei. The equatorial and axial endocyclic methylene protons are displayed as complex multiplet patterns. The four ethylene hydrogens give rise to an AA′XX′ pattern in the ^1H NMR spectrum of the carbonylethene complex **8**. This is slightly broadened by additional interactions with the phosphorus nuclei. The chemical shifts of the ethylene multiplet are basically invariant to changes in temperature from -105°C to $+55$°C. This indicates that the two different environments for the hydrogen atoms do not change over this temperature range. The ^{13}C singlet resonance of the carbon atoms of the coordinated ethylene ligand is shifted intensely to higher field in comparison with free ethene ($\Delta\delta = 98.2$ ppm) and is not effected by changes of temperature. The AA′XX′ pattern of the ethylene protons and the single resonance of the ethylene carbon atoms suggest a rigid C_S symmetry for the complex. In contrast to the rigid behavior of ethylene ligand the NMR data for the tripodal phosphine backbone are in agreement with high fluxionality of the [Ir(tdppcymome)] fragment. Thus in the ^1H NMR spectrum only one set of an ABX_2X' pattern is observed for the ring methylene protons. Further support for a dynamic process which equilibrates the equatorial and apical positions of the ligand backbone in **8** stems from $^{31}P\{^1H\}$ NMR investigations at variable temperatures. The broad unresolved resonance at $\delta = -9.0$ which is found at room temperature already indicates that the exchange process is slow. The coalescence point is reached at 14°C. With decreasing temperature two broad signals in a 2:1 ratio are observed until at -31°C the low field resonance displays a broad doublet and the high field part is fully resolved into a triplet (Fig. 1). The AB_2 spin pattern corresponds to the trigonal bipyramidal structure with C_S symmetry. At this point a second dynamic process starts with a lower energy barrier. At temperatures below -34°C the doublet of the two equatorial phosphine groups further broadens and then coalesces at -66°C. On the contrary the lineshape of the high field multiplet due to the phosphorus *trans* to CO remains sharp. Further cooling reveals two broad signals (1:1) which finally can be resolved at -105°C as two doublets of doublets. This *gives* evidence of a completely distorted molecule.

The NMR spectra of the carbonylchlorohydrido complexes **5**,**5′**, the carbonyldihydrido complex **7**,**7′** and the orthometalated carbonylhydrido complex **9** are in agreement with rigid, octahedral structures with *facial* coordination of the ligand. In the $^{31}P\{^1H\}$ NMR spectra of the C_1 symmetric complexes **5**,**5′** both compounds give rise to three doublets of doublets of the three inequivalent phophorus nuclei in the range of 0 to -11 ppm. The $^2J_{PP}$ coupling constants of 10.6 and 22.8 Hz are characteristic for the *cis* arrangements of the phosphine groups. The formation of a four membered irida-phospha-cyclobutene ring during the intramolecular oxidative addition of a phenyl C–H bond to the $[Ir(tdppcymome)(CO)]^+$ fragment results in C_1 symmetry of the octahedral complex **9**. Thus the $^{31}P\{^1H\}$ NMR spectrum of **9** gives rise to three doublets of doublets (*cis* $^2J_{PP}$ 16.8 and 23.5 Hz) consistent with three environmentally different phosphorus atoms. For the phosphorus nucleus which is incorporated into the orthometalated ring an obvious high-field shift ($\delta - 80.5$) is observed. The ^1H NMR spectra of the compounds **5**, **5′**, and **9** display a doublet of doublets of doublets in the hydride region [$\delta - 9.15$ (**5**, **5′**) and -8.74 (**9**)] which is the result of one large coupling of the hydride resonance to one phosphine group *trans* and two small couplings by two phosphine groups *cis* to the hydride. The diastereotopic protons of the endocyclic methylene groups are observed as broad overlapping multiplets. The exocyclic ones give three overlapping ABX patterns. The methyl groups are observed as three singlets. In the $^{31}P\{^1H\}$ NMR spectrum of the C_S symmetric compound **7** the $^2J_{PP}$ couplings of the inequivalent phosphorus nuclei lead to a doublet and a triplet. According to the stronger *trans* influence of the hydride compared to CO the doublet of the phosphine groups *trans* to the hydrogen ligands is observed at a higher field than the triplet of the phosphine group *trans* to CO. The hydride region in the ^1H NMR spectrum displays the AA′ part of an AA′MXX′ spin system which is typical for two chemically but not magnetically equivalent hydride ligands. The diastereotopic protons of the exocyclic methylene groups show one doublet and two ABX patterns. The methyl protons are indicated by two singlets in a 2:1 ratio.

2.3. EXAFS studies on complexes **1–4**

The pentacoordinate iridium complexes **1–3** are difficult to crystallize and thus crystallographic data are not easily accessible. The EXAFS measurements performed on powders of **1–4** lead to the coordination

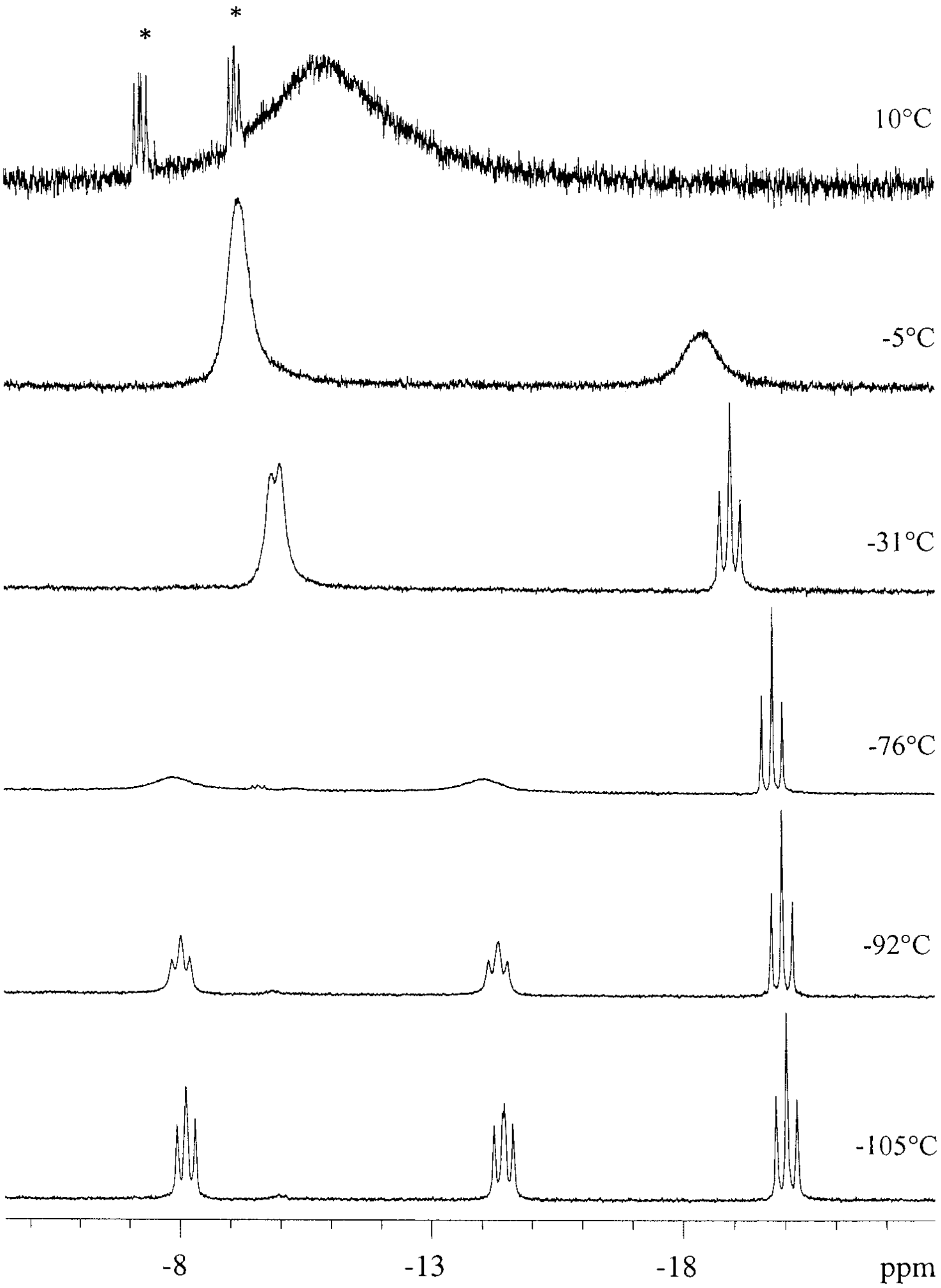


Fig. 1. Variable temperature $^{31}P\{^1H\}$ NMR spectra of compound **8** (161.98 MHz). The asterisks denote the decomposition product **9**.

Table 1
Bond distances [Å] and angles [°] of the complexes **1–4** as obtained from EXAFS investigations

	N	**1** (H)	$2\sigma^2$ [Å^2]	**2** (COOCH$_3$)	$2\sigma^2$ [Å^2]	**3** (CN)	$2\sigma^2$ [Å^2]	**3** (CN)[a]	**4** (CH$_2$OCH$_3$)	$2\sigma^2$ [Å^2]
Ir–C	1	1.84	0.028	1.91	0.029	1.88	0.028	1.880(5)	1.79	0.028
Ir–P	1	2.29	0.007	2.27	0.007	2.27	0.007	2.267(2)	2.29	0.007
Ir–P	2	2.37	0.018	2.35	0.020	2.35	0.018	2.352(2)	2.35	0.018
Ir–Cl	1	2.47	0.013	2.43	0.012	2.43	0.013	2.429(2)	2.43	0.013
Ir–O	1	3.00	0.029	3.03	0.030	3.01	0.029	3.013(5)	3.00	0.029
Ir–C–O		177		175		174		173.6(6)	179	
Ir–C[b]	6	4.24	0.006	4.23	0.013	4.20	0.011		4.22	0.017
Ir–C[b]	6	4.45	0.003	4.43	0.010	4.42	0.007		4.43	0.017

[a] X-ray structure determination [7].

[b] For reason of completeness the average distances of the carbon atoms, which can be assigned to the cyclohexane atoms and the *ipso* carbon atoms of the phenyl groups at the phosphorus atoms, are given.

numbers of the iridium atoms and to the distances of the atoms round the metal centers (Table 1). In all four cases the EXAFS function can be described completely by the assumption of three phosphorus atoms, two with a long Ir–P distance (2.37 Å) and one short Ir–P bond length (2.29 Å), one chlorine and one CO group in the coordination sphere of iridium. This is consistent with a trigonal bipyramidal geometry where two diphenylphosphino groups occupy the equatorial and one the axial position. In the case of compound **3**, which has a polycrystalline structure, the EXAFS data were confirmed by the results of an X-ray structure determination [8]. The linear carbonyl groups make the use of difficult multiple scattering calculations necessary, from which the indirect iridium–oxygen distances are obtained. On the other hand this formalism leads to the bond angle between iridium, carbon and oxygen. The analysis of the experimental data show, that in the compounds **1–4** these angles differ, although an error range of about 1.5° can be discussed for these values. For compounds **2** and **3** the obtained bond angle differ from the expected 180° for a linear carbonyl group. The influence of multiple scattering in the Fourier transform is shown in Fig. 2.

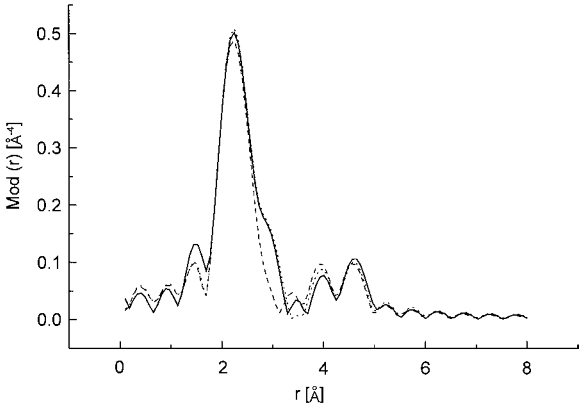


Fig. 2. Fourier transforms of the $\kappa^3 \cdot \chi(k)$ functions of **4**. Experimental (solid line) and theoretical calculated functions considering single (dashed line) and multiple scattering (dotted line).

3. Conclusion

The influence of the functional groups on the ν(CO) absorption of the complexes **1–4** is displayed in Fig. 3. With increasing group electronegativity [13] of the functional group the ν(CO) absorption is shifted to higher frequencies. The near linearity of the graph leads to the conclusion that the electron density at the metal center is controlled by the inductive capability of the functional groups. According to this the basicity [14] of the Ir(tripod)(CO)Cl complexes decrease in the order **1** > **4** > **2** > **3** which is reflected by their reactivity towards acids [9]. In contrast, from the stability of the olefin complexes [Ir(tripod)(CO)(C$_2$H$_4$)]BPh$_4$ which follows the order of the ligands tdppcymome ≤ tdppcyme < tdppcy < tdppcycn it can be concluded that steric reasons also play an important role in the reactivity of the Ir(tripod) complexes. The temperature dependent ^{31}P NMR spectra of these complexes also indicate that the functional groups at the ligand backbone lead to a considerable distortion of the molecules in the case of the tdppcymome, tdppcyme and tdppcycn ligands, re-

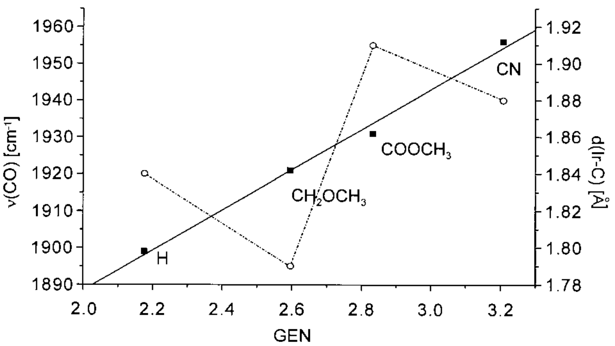


Fig. 3. ν(CO) absorptions (■ solid line) and Ir–C distances (○ dashed line) of **1–4** as function of the group electronegativity (GEN).

spectively [9]. Steric reasons may therefore be responsible that the correlation of the Ir–C bond length vs. GEN does not follow the one of ν(CO) vs. GEN.

4. Experimental

4.1. General comments

All reactions were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were distilled under Ar; benzene, toluene, diethylether, and THF were distilled from Na/Ph_2CO; *n*-pentane and *n*-hexane were distilled from $LiAlH_4$; dichloromethane was distilled from CaH_2. The gases H_2, CO, and C_2H_4 were of commercial grade and used without further purification. The phosphine ligand *cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxy methyl)cyclohexane [10] and $Ir(PPh_3)_2(CO)Cl$ [15] were prepared as described in the literature. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DRX 250 or a Bruker AMX 400 operating at 250.13 or 400.13 and 62.90 or 100.62 and 101.26 or 161.98 MHz, respectively. ^1H chemical shifts were referenced to the residual proton peaks of the solvents vs. TMS. ^{13}C chemical shifts were calibrated against the deuterated solvent multiplet relative to TMS. ^{31}P chemical shifts were measured relative to external 85% H_3PO_4 with downfield values taken as positive. In addition to the $^{13}C\{^1H\}$ NMR spectrum a ^{13}C-DEPT [16] experiment was routinely performed for each compound. The assignments of the ethylene group in **8** was supported by $^1H/^{13}C$ 2D HMQC [17] experiments using standard Bruker software. ^1H, ^{13}C, and ^{31}P DNMR experiments were carried out on a Bruker AMX 400. The temperature was measured using the temperature control unit Eurotherm and an external thermocouple (Pt 100). Infrared spectra were recorded on a Bruker IFS 48. Mass spectra (FD) were detected on a Finnigan MAT 711 A modified by AMD; FAB Finnigan MAT TSQ70. Elemental analysis were performed using a Carlo Erba model 1106 elemental analyzer. Conductivities were measured on WTW, model DIGI 610 connected to a conducting cell LTA/S. The conductivity data were obtained at sample concentrations of 1 mmol in dichloromethane solutions at room temperature. The EXFAS measurements were carried out at beamline ROEMO II at HASYLAB at DESY, Hamburg, at the iridium L(III)-edge with a Si⟨311⟩ double crystal monochromator. Data were recorded in a typical transmission geometry, using three ionization chambers for monitoring I_0, I_1, and I_2. An iridium foil (thickness 20 μm) was used for energy calibration, which was controlled with the third ionization chamber. The samples itself were prepared by pressing a mixture of 40 mg **1–4** and 50 mg of polyethylene to a tablet of a diameter of 1.0 cm and a thickness of 2.5 mm. The data were analyzed with a program package, specially developed for requirements of amorphous samples, which is described in detail elsewhere [18]. In the first step background absorption was removed from experimental absorption spectrum by subtraction of a Victroreen-type polynomial. Then the background subtracted spectrum was convoluted with a series of increasingly broader Gauss functions and the common intersection point of the spectra, broadened by convolution, was used to define the threshold energy E_0. To determine the smooth part of the background subtracted spectrum, a modified smoothing spline algorithm was used. The data analysis in k space was performed according to the curved wave multiple scattering formalism with the program EXCURV90 [19]. The number of parameters that were determined corresponds to the number of independent data points and the test of Joyner et al. [20] was applied.

4.2. Carbonylchloro[cis,cis-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxymethyl)cyclohexane]iridium(I) (**4**)

A solution of 769 mg (1.0 mmol) of tdppcymome and 780 mg (1.0 mmol) of $Ir(PPh_3)_2(CO)Cl$ in 30 ml toluene was stirred at 80°C for 1.5 h. 150 ml of *n*-heptane was added dropwise to the red suspension at 80°C over a period of 1.5 h. After being cooled to room temperature, the orange precipitate was collected on a sintered-glass frit (P4), washed five times with 10 ml of *n*-pentane each, and dried in vacuo. Yield: 871 mg (85%). Mp: 250°C (dec.). IR (KBr, cm^{-1}): 1920 ν(CO); (CH_2Cl_2, cm^{-1}): 1921 ν(CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 8.8$ (s). ^1H NMR (CD_2Cl_2): $\delta = 2.01$–2.24 [m, 3 H, CHH_e], 2.51–2.86 [m, 3 H, CHH_a], 3.32 [s, 9 H, CH_2OCH_3], 3.68 [br. s, 6 H, CH_2OCH_3], 7.02–7.45 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 31.43$ [m, CH_2], 38.35–39.28 [br. m, CP], 59.07 [s, CH_2OCH_3], 77.49 [s, CH_2OCH_3], 127.26–127.41 [m, *meta*-C_6H_5], 129.30 [s, *para*-C_6H_5], 133.57–134.64 [m, *ipso*-C_6H_5], 135.89–136.08 [m, *ortho*-C_6H_5]. MS (FD), m/z: 996.1 [M^+-CO]. Calcd. for $C_{49}H_{51}ClIrO_4P_3$ (1024.53): C 64.56, H 5.42. Found: C 64.13, H 5.38.

4.3. Reactions of **4** with HBF_4 and NH_4PF_6

To a solution of **4** in 50 ml of CH_2Cl_2 was added 0.1 ml of an aqueous solution of HBF_4 (8 M) or 1 ml of an aqueous solution of NH_4PF_6 (1 M). The reaction mixture was stirred for 15 h at room temperature. The aqueous phase was removed, the organic phase was concentrated in volume to 3 ml, and 50 ml of *n*-pentane was added. The resulting off-white precipitate was filtered off, washed three times with 10 ml of *n*-pentane each, and dried under reduced pressure.

*4.4. Carbonylchlorohydrido[cis,cis-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxymethyl)cyclohexane] iridium(III) tetrafluoroborate (**5**)*

IR (CH_2Cl_2, cm^{-1}): 2161 w ν(IrH), 2083 st ν(CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = -10.9$ [dd, $^2J_{PP} = 22.8$ Hz, $^2J_{PP} = 10.6$ Hz, P *trans* to H], -5.4 [dd, $^2J_{PP} = 22.8$ Hz, $^2J_{PP} = 22.8$ Hz, P], -0.2 [dd, $^2J_{PP} = 22.8$ Hz, $^2J_{PP} = 10.6$ Hz, P].

*4.5. Carbonylchlorohydrido[cis,cis-1,3,5-tris(diphenyl phosphino)-1,3,5-tris(methoxymethyl)cyclohexane]iridium(III)hexafluorophosphate (**5′**)*

The amount of 204.9 mg (0.20 mmol) of **4** was used. Yield: 208.3 mg (89%). Mp: > 163°C (dec). IR (KBr, cm^{-1}): 2158 w ν(IrH), 2080 st ν(CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = -143.2$ [sept., $^1J_{PF} = 710.5$ Hz], -10.9 [dd, $^2J_{PP} = 22.8$ Hz, $^2J_{PP} = 10.6$ Hz, P *trans* to H], -5.5 [dd, $^2J_{PP} = 22.8$ Hz, $^2J_{PP} = 22.8$ Hz, P], -0.1 [dd, $^2J_{PP} = 22.8$ Hz, $^2J_{PP} = 10.6$ Hz, P]. ^1H NMR (CD_2Cl_2): $\delta = -9.15$ [ddd, $^2J_{PH} = 138.82$ Hz, $^2J_{PH} = 10.38$ Hz, $^2J_{PH} = 10.38$ Hz, 1 H, IrH], 2.20–3.23 [m, 6 H, CH_2], 3.27, 3.35, 3.37 [s, 9 H, CH_2OCH_3], 3.57–3.88 [m, 6 H, CH_2OCH_3], 6.93–7.61 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 31.18$–31.30, 31.47–31.63, 32.23–32.32 [m, CH_2], 36.82, 37.25, 38.19 [d, $^1J_{PC} = 7.55$, 11.95, 25.16 Hz, CP], 59.12, 59.22 [s, CH_2OCH_3], 76.13, 77.60, 77.75 [s, CH_2OCH_3], 123.73–137.97 [m, C_6H_5], 166.65 [ddd, $^2J_{PC} = 119.50$, $^2J_{PC} = 6.29$, $^2J_{PC} = 6.29$ Hz, CO]. Λ_M (CH_2Cl_2, 25°C, cm^2 Ω^{-1} mol^{-1}): 43.1. MS (FAB), m/z: 1025.6 [M^+-PF_6^-]. Calcd. for $C_{49}H_{52}ClF_6IrO_4P_4$ (1170.50): C 50.28, H 4.48, Cl 3.03, F 9.74. Found: C 49.89, H 4.41, Cl 2.88, F 9.52.

*4.6. General procedure for the reactions of **4** with H_2, CO and C_2H_4*

A solution of 204.9 mg (0.20 mmol) of **4** in 50 ml of CH_2Cl_2 was degassed by using the freeze–pump–thaw technique. To the frozen solution at -90°C was added one of the gases (1.3 bar) H_2, CO, and C_2H_4, respectively. After the reaction mixture had been allowed to warm to room temperature it was stirred for 16 h. The solvent was concentrated in volume to 3 ml, and 50 ml of *n*-pentane was added. The resulting off-white precipitate was filtered off, washed three times with 10 ml of *n*-pentane each, and dried under reduced pressure.

*4.7. Dicarbonyl[cis,cis-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxymethyl)cyclohexane]iridium(I) chloride (**6**)*

Yield: 245.7 mg (92%). Mp: > 174°C (dec). IR (KBr, cm^{-1}): 2035 st, 1957 st ν(CO); (CH_2Cl_2, cm^{-1}): 2050, 1977 ν(CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = -2.3$ [s]. ^1H NMR (CD_2Cl_2): $\delta = 2.28$–2.43 [m, 3 H, CHH_e], 2.67–3.09 [m, 3 H, CHH_a], 3.33 [s, 9 H, CH_2OCH_3], 3.68 [d, $^3J_{PH} = 3.78$ Hz, 6 H, CH_2OCH_3], 7.13–7.41 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 32.25$–32.40 [m, CH_2], 38.61 [dt, $^1J_{PC} = 25.16$, $^3J_{PC} = 8.33$ Hz, CP], 59.21 [s, CH_2OCH_3], 76.83 [s, CH_2OCH_3], 128.22–135.16 [m, C_6H_5], 180.15 [q, $^2J_{PC} = 22.64$ Hz, CO]. Λ_M (CH_2Cl_2, 25°C, cm^2 Ω^{-1} mol^{-1}): 42.4. MS (FAB), m/z: 1017.1 [M^+-Cl^-], 989.2 [M^+–Cl^-–CO]. Calcd. for $C_{50}H_{51}ClIrO_5P_3$ (1052.54): C 57.06, H 4.88, Cl 3.37. Found: 56.81, H 5.16, Cl 3.82.

*4.8. Carbonyldihydrido[cis,cis-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxymethyl)cyclohexane]iridium(III) chloride (**7**)*

Yield: 227.2 mg (93%). Mp: > 174°C (dec). IR (KBr, cm^{-1}): 2091 m ν(IrH), 2045 st ν(CO); (CH_2Cl_2, cm^{-1}): 2058 ν(CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = -3.5$ [d, $^2J_{PP} = 23.5$ Hz, P *trans* to H], -0.6 [t, $^2J_{PP} = 23.5$ Hz, P *cis* to H]. ^1H NMR (CD_2Cl_2): $\delta = -10.46$ [AA′MXX′, 2 H, IrH], 2.07–2.34 [m, 3 H, CHH_e], 2.55–2.97 [m, 3 H, CHH_a], 3.33, 3.37 [s, 9 H, CH_2OCH_3], 3.63 [d, $^3J_{PH} = 4.63$ Hz, 2 H, CH_2OCH_3], 3.67 [ABX, $^2J_{HH} = 9.57$, $^3J_{PH} = 3.65$ Hz, 2 H, CH-$HOCH_3$], 3.75 [ABX, $^2J_{HH} = 9.57$, $^3J_{PH} = 3.65$ Hz, 2 H, $CHHOCH_3$], 7.07–7.64 [m, 30 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 30.58$–31.02 [m, CH_2], 37.41–38.21 [m, CP], 59.15, 59.19 [s, CH_2OCH_3], 76.80–77.21 [s, CH_2OCH_3], 128.30–135.48 [m, C_6H_5], 170.41 [dt, $^2J_{PC} = 98.88$, $^2J_{PC} = 8.03$ Hz, CO]. Λ_M (CH_2Cl_2, 25°C, cm^2 Ω^{-1} mol^{-1}): 41.3. MS (FAB), m/z: 991.1 [M^+-Cl^-]. Calcd. for $C_{49}H_{53}ClIrO_4P_3$ (1026.55): C 57.33, H 5.20, Cl 3.45. Found: C 56.79, H 5.02.

*4.9. Carbonylethene[cis,cis-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxymethyl)cyclohexane]iridium(I) tetraphenylborate (**8**)*

In addition the amount of 75.3 mg (2.2 mmol) of $NaBPh_4$ was added. Reaction time: 10 h. The reaction mixture was separated from NaCl and residual $NaBPh_4$ and the work up was followed as described in the general procedure. Yield: 232.0 mg (87%). Mp: > 185°C (dec). IR (KBr, cm^{-1}): 2032 st ν(CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 21°C): $\delta = -9.0$ [br. s]. ^1H NMR (CD_2Cl_2, 21°C): $\delta = 2.05$, 2.49 [AA′XX′, N = 7.2 Hz, 4 H, C_2H_4], 2.29 [ABX_2, $^2J_{HH} = 16.58$, $^3J_{PH} = 15.26$ Hz, 3 H, CHH_e], 2.83 [ABX_2, $^2J_{HH} = 16.58$, $^3J_{PH} = 36.10$ Hz, 3 H, CHH_a], 3.33 [s, 9 H, CH_2OCH_3], 3.66 [s, 6 H, CH_2OCH_3], 6.87–7.42 [m, 50 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 21°C): $\delta = 25.10$ [s, C_2H_4], 32.04 [s, CH_2], 38.75 [d, $^1J_{PC} = 24.45$ Hz, CP], 59.29 [s, CH_2OCH_3], 77.47–77.61 [m, CH_2OCH_3], 122.22–

136.38 [m, C_6H_5], 164.57 [q, $^1J_{CB} = 48.73$ Hz, *ipso*-$B(C_6H_5)_4^-$]. Λ_M (CH_2Cl_2, 25°C, cm^2 Ω^{-1} mol^{-1}): 41.1. MS (FAB), m/z: 1017.3 [M^+-$B(C_6H_5)_4^-$]. Calcd. for $C_{75}H_{75}BIrO_4P_3$ (1336.38): C 67.41, H 5.65. Found: C 65.16, H 5.32.

4.10. *Carbonylhydrido[cis,cis-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxymethyl)cyclohexane] iridium(III)tetraphenylborate* (**9**)

To a solution of 204.9 mg (0.20 mmol) of **4** in 50 ml of dichloromethane 75.3 mg (0.22 mmol) of $NaBPh_4$ was added. The suspension was stirred at room temperature for 16 h. NaCl and residual $NaBPh_4$ were separated by filtration. The solution was concentrated to 3 ml in volume, 50 ml of *n*-pentane was added, and the resultant precipitate was filtered off, washed three times with 10 ml of *n*-pentane each, and dried in vacuo. Yield: 230.3 mg (88%). Mp: > 183°C (dec). IR (KBr, cm^{-1}): 2080 w ν(IrH), 2035 st ν(CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = -80.5$ [dd, $^2J_{PP} = 23.5$ Hz, $^2J_{PP} = 16.8$ Hz, P *ortho*-C], -7.0 [dd, $^2J_{PP} = 16.8$ Hz, $^2J_{PP} = 16.8$ Hz, P *trans* to H], -5.5 [dd, $^2J_{PP} = 23.5$ Hz, $^2J_{PP} = 16.8$ Hz, P]. ^1H NMR (CD_2Cl_2): $\delta = -8.74$ [ddd, $^2J_{PH} = 123.81$ Hz, $^2J_{PH} = 14.63$ Hz, $^2J_{PH} = 9.02$ Hz, 1 H, IrH], 2.07–3.61 [m, 6 H, CH_2 and 3 H, CH_2OCH_3], 3.21, 3.29, 3.33 [s, 9 H, CH_2OCH_3], 3.78 [ABX, $^2J_{HH} = 9.51$, $^3J_{PH} = 3.29$, 1 H, $CHHOCH_3$], 3.85 [ABX, $^2J_{HH} = 9.18$, $^3J_{PH} = 2.66$, 1 H, $CHHOCH_3$], 4.17 [ABX, $^2J_{HH} = 9.51$, $^3J_{PH} = 3.25$, 1 H, $CHHOCH_3$], 6.79–7.58 [m, 49 H, C_6H_5]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 31.00$–31.17, 32.82–32.95, 36.74–36.90 [m, CH_2], 36.78, 39.05, 39.77 [d, $^1J_{PC} = 25.35$, 21.07, 27.52 Hz, CP], 59.01, 59.25, 59.33 [s, CH_2OCH_3], 75.72 [br. s, CH_2OCH_3], 78.13, 79.76 [d, $^1J_{PC} = 2.36$, 5.20 Hz, CH_2OCH_3], 122.03–137.51 [m, C_6H_5], 147.71 [ddd, $^2J_{PC} = 63.02$, $^2J_{PC} = 5.79$, $^2J_{PC} = 5.79$ Hz, IrC], 164.30 [q, $^1J_{CB} = 49.33$ Hz, *ipso*-$B(C_6H_5)_4^-$], 171.60 [ddd, $^2J_{PC} = 90.76$, $^2J_{PC} = 7.20$, $^2J_{PC} = 4.17$ Hz, CO]. Λ_M (CH_2Cl_2, 25°C, cm^2 Ω^{-1} mol^{-1}): 44.8. MS (FAB), m/z: 989.1 [M^+-$B(C_6H_5)_4^-$]. Calcd. for $C_{73}H_{71}BIrO_4P_3$ (1308.32): C 67.02, H 5.47. Found: C 67.52, H 5.68.

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