An iridium-mediated C–H activation/CO_2-carboxylation reaction of 1,1-bisdiphenylphosphinomethane†

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The reaction of 1,1-bisdiphenylphosphinomethane (dppm, 4 eq.) with $[IrCl(coe)_2]_2$ results in a solvent dependent equilibrium from which the complexes [IrCl(dppm)(dppm-H)(H)] (**1**) and $[Ir(dppm)_2]Cl$ (**2**) were isolated. When **2** is dissolved in methanol, $[IrCl(dppm)_2(H)][OCH_3]$ (**4**) is formed as dominant species in solution. The C–H activation reaction which leads to **1** and **4** can be suppressed by adding an additional dppm ligand per iridium center resulting in the formation of $[Ir(dppm)_3]Cl$ (**5**). If the reaction of dppm with $[IrX(coe)_2]_2$ (X = Cl, I) is performed under an atmosphere of CO_2 the complexes $[IrX(dppm)(H)\{(Ph_2P)_2C–COOH\}]$ (**6**: X = Cl; **7**: X = I) are formed by a CH activation/CO_2 carboxylation sequence. The reaction of **6** with NH_4PF yields $[IrCl(dppm)_2(H)]PF_6$.(**10**). Additionally the lithium compounds $[Li(dme)_2(dppm-H)]$ (**3**) and $[Li(dme)\{(Ph_2P)_2CHCOO\}]_2$ (**8**) were prepared for comparison. The molecular structures of the compounds **1**, **3**, **5**, **7**, **8** and of the related iridium complex $[IrCl(dppm)_2(H)]I$ (**11**) are reported.

Introduction

The use of CO_2 as renewable, cheap and non-toxic carbon source is highly desirable but limited by its high stability and low reactivity. For instance, the direct carboxylation of hydrocarbons with CO_2 is a straightforward route to carboxylic acids. Besides the reaction of CO_2 with strong carbon nucleophiles like Grignard reagents, the transition metal mediated oxidative coupling of unsaturated hydrocarbons with CO_2 offers an attractive route to such acids or their derivatives. Electrochemical or photochemical activation offer additional ways to initiate a reaction between CO_2 and hydrocarbons.[1]

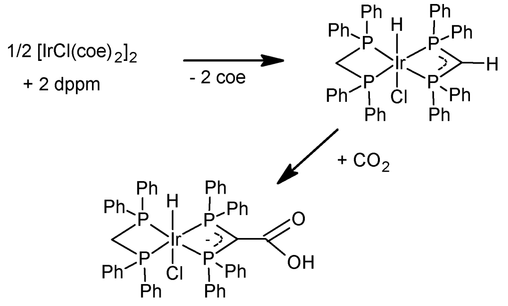
In case of aromatic hydrocarbons a carboxylation with CO_2 can be achieved under either basic or acidic conditions.[2,3] The production of hydroxybenzoic acid derivatives from the related alkali metal phenoxides (Kolbe–Schmitt reaction)[4–6] is one of the rare examples of a synthesis using CO_2 as a carbon source in industrial scale. Additionally, related alkali metal phenoxides have been used as CO_2 transfer agents in the carboxylation of C–H acidic compounds.[7–11]

The carboxylation of less or none activated alkanes requires more forcing conditions. The vanadium catalyzed carboxylation of methane with CO_2 in fuming H_2SO_4 to form acetic acid in presence of $K_2S_2O_8$ as oxidizing agent was reported.[12,13]

The transition metal mediated C–H activation followed by carboxylation using CO_2 may offer an alternative approach under milder conditions. Various iridium compounds are known to be active in such C–H activation reactions[14] and several examples for CO_2 activation by this metal have been reported,[1] too, making iridium complexes a promising choice for further studies.

English and Herskovitz demonstrated that iridium compounds are able to mediate the carboxylation of acetonitrile by CO_2,[15] but the formed products were not isolated. Later Behr *et al.* observed a similar reactivity, using the more acidic malonodinitrile (pK_a = 12) as substrate. In this case, several iridium compounds containing the anion $[HOOCC(CN)_2]^-$ were isolated and completely characterized.[16,17]

We preliminary reported the iridium mediated transformation of the less acidic dppm (1,1-bisdiphenylphosphinomethane, pK_a = 29.9 [18]) into the unpredicted anionic ligand $[(Ph_2P)_2C–COOH]^-$ *via* a C–H activation/carboxylation sequence (see Scheme 1).[19]



Scheme 1

Herein more detailed results will be given.

Results

The C–H activation of dppm

The reaction of dppm with $[Ir_2(\mu-Cl)_2(coe)_4]$ (coe = cyclooctene) in a 4 to 1 ratio was first described by Cowie and coworkers.[20] The product obtained from the reaction in benzene was

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recrystallized from CH_2Cl_2 and identified as the pentacoordinated iridium(I) complex [IrCl(dppm)$_2$] on basis of its NMR data. Later on, Tejel *et al.* found that this species exists in solution in a solvent dependent equilibrium with an iridium(III) compound formed *via* C–H activation of one of the dppm ligands.[21] They isolated [IrCl(dppm)(dppm-H)(H)] (dppm-H = 1,1-bisdiphenylphosphinomethanide) from a toluene solution. Reinvestigation of this equilibrium in various nonchlorinated solvents confirmed the existence of [IrCl(dppm)(dppm-H)(H)] (**1**) while [IrCl(dppm)$_2$] was not directly observed under the applied conditions. However, the red, ionic compound [Ir(dppm)$_2$]Cl (**2**) was instead identified as the dominating species in more polar solvents like acetone and acetonitrile. Compound **1** can be obtained in crystalline form from toluene [19] or dimethoxy ethane (dme). The molecular structure is shown in Fig. 1.

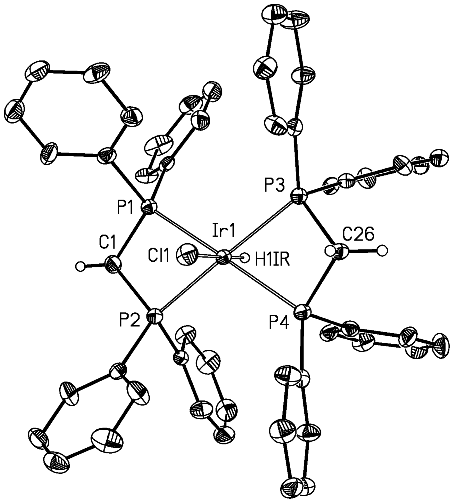


Fig. 1 Molecular structure of **1** (most of the H-atoms and cocrystallized dme are omitted for clarity). Selected distances (Å) and angles (°) are: Ir1–P1 2.3333(19), Ir1–P2 2.330(2), Ir1–P3 2.3300(19), Ir1–P4 2.3273(19), Ir1–Cl 2.5129(18), P1–C1 1.724(8), P2–C1 1.720(8), P3–C26 1.852(7), P4–C26 1.855(8), P1–Ir1–P4 174.71(7), P2–Ir1–P3 174.21(7), P1–C1–P2 100.0(4), P3–C26–P4 93.3(4).

Like in related diphosphanylmethanide complexes, the formed four membered ring Ir1,P1,C1,P2 is planar.[22,23] The observed distances Ir1–P1 (2.333(19) Å) and Ir1–P2 (2.330(2) Å) are slightly longer than found in [Ir(dppm-H)(H)(tp)] (2.276 and 2.269 Å).[24] The narrow angle of the ligand backbone P1–C1–P2 of 100.0(4) reflects the high orbital contribution in the ligand bonding resulting in compression of this angle to achieve better overlapping of the phosphorus lone pair with iridium based orbitals.

In order to further address this aspect the lithium complex [Li(dme)$_2$(dppm-H)] (**3**) was prepared from [Li(dppm-H)]$_n$.[25] The use of the harder lithium should result in a lower affinity to the soft phosphorus donor atoms and overall in a decreased orbital contribution in ligand bonding.

In **3**, the lithium atom is also in an octahedral coordination sphere (see Fig. 2) but the coordinated diphosphanylmethanide ligand shows some remarkable differences. The more electrostatic nature of the ligand bonding leads to an opening of the backbone angle of the dppm-H ligand to 114.46° while the P–C bonds (1.731 Å) are only slightly longer then in **1** (av. 1.722 Å). The distance Li–P(1) of 2.896(3) Å is huge and suggests that **3** should be treated rather as a contact ion pair than as a covalently bound molecule. Besides **3** other solvent adducts of [Li(dppm-H)]$_n$ for instance with thf or tmeda are known.[26,27,28]

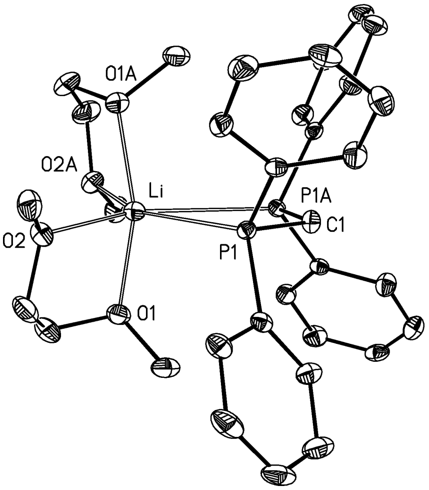


Fig. 2 Molecular structure of **3** (H-atoms are omitted for clarity). Selected distances (Å) and angles (°) are: Li–P1 2.896(3), Li–O1 2.1184(12), Li–O2 2.114(2), P1–C1 1.7308(11), O1–Li–O2 80.43(7), O1–Li–P1 100.31(8), P1–Li–P1A 60.35(7), P1–C1–P1A 114.46(11).

While the colourless iridium(III) complex **1** was easily obtained in pure form from various solvents, the isolation of the related red iridium(I) compound **2** was found to be more challenging. The use of more polar solvents like acetone or acetonitrile shifts the equilibrium towards **2** as indicated by the formation of dark red solutions from the reaction of dppm and [Ir$_2$(μ-Cl)$_2$(coe)$_4$]. However, only crystals of **1** were obtained upon cooling. Finally the use of ethanol enables the isolation of **2**. Although red crystals of **2** were obtained several times as described below (see experimental section) the given procedure tends to be somewhat irreproducible. Since the iridium(I) species formed slowly reacts with ethanol at room temperature, rapid crystallization is necessary, but the reaction mixture tends to oversaturate. In such cases dominantly iridium(III) hydrido complexes are formed by dehydrogenation of the alcohol.

Once isolated, **2** is only sparingly soluble in thf due to its ionic nature. The crystals show dichroism (red/greenish brown) and a red luminescence when irradiated with UV radiation (366 nm) like previously reported for a similar compound containing the cation [(dppm)$_2$Ir]$^+$.[21,29] Unfortunately, the crystals isolated from ethanol were not suitable for X-ray measurement. When those crystals were dissolved in a mixture of ethanol and d$_8$-THF the ^{31}P NMR spectrum shows two singlets at $\delta = -35.7$ and -53.9. The signal first mentioned which slowly decreases in intensity was assigned to **2** by comparison with the values reported for related compounds containing the same cation (see compound **9** and [30]). The second signal belongs to the compound [[IrCl(dppm)$_2$(H)]$^+$[OEt]$^-$ (**4a**) which most likely results from deprotonation of ethanol by **1** formed as an intermediate from **2**. While in ethanol this reaction is rather slow, which allowed the isolation of **2** in the first place, the use of more acidic methanol as solvent results in rapid formation of a pale yellow solution which contains [IrCl(dppm)$_2$(H)]$^+$[OMe]$^-$ (**4b**) as sole product. The reaction of **2** in d$_4$-methanol indicates that there still is an equilibrium between **1** and **4** as shown by the rapid exchange of all protons of the P–CH$_2$–P groups

Table 1 Comparison of selected bond lengths and angles of the iridium complexes **1**, **5**, **11** and the lithium complex **3**

	chelating dppm			*dppm-H*			*others*	
	M–P (av.) [Å]	P–C (av.) [Å]	P–C–P (av.) [°]	M–P (av.) [Å]	P–C (av.) [Å]	P–C–P [°]	Distances [Å]	Bonds
Ir complexes								
1	2.329(2)	1.854(8)	93.3(4)	2.332(2)	1.722(8)	100.0(4)	2.513(2)	Ir1–Cl1
5	2.334(2)	1.843(5)	95.2(2)	—	—	—	2.360(2)	Ir1–P5
11	2.330(3)	1.841(13)	94.6(5)	—	—	—	2.467(3)	Ir1–Cl1
[IrH(dppm-H)(Tp)][24]				2.2724(13)	1.727(5)	97.5(3)		
Li complex								
3	—	—	—	2.896(3)	1.731(1)	114.5(1)	2.116(2)	Li–O (av.)

by deuterium, while the hydride signal is not affected. The irreversible formation of [IrCl(dppm)$_2$(H)]$^+$[OH]$^-$ by the reaction of **1** and H$_2$O was previously reported.[21] The formation of **1** and **4** from the iridium(I) compound **2** in methanol can be suppressed by adding an additional equivalent of dppm. From the resulting orange coloured solution, crystals of the 18VE complex [Ir(dppm)$_3$]Cl·6MeOH (**5**) were isolated.

Despite the broad range of application of dppm in transition metal chemistry, only a few mononuclear tris(dppm) complexes of the general formula [M(dppm)$_3$]$^{n+}$ have been reported so far. Besides the crystal structures of two rhenium compounds, containing the cation [Re(dppm)$_3$]$^+$ with three chelating dppm ligands (anions: I$^-$ or ReO$_4^-$),[31,32] only the crystal structure of the tetrahedral nickel compound [Ni(dppm)$_3$] with one chelating and two monodentate dppm ligands is known.[33]

As shown in Fig. 3, the iridium(I) atom in compound **5** is in a distorted trigonal bipyramidal environment with two chelating dppm ligands and an additional monodentate one. The phosphorus atoms P1 and P3 as well P5 of the monodentate dppm are in equatorial positions while P2 and P4 adopt the axial positions with an angle of 165.51° between them. The iridium phosphorus distances range from 2.2989(13) (Ir–P3) to 2.3896(13) Å (Ir–P1). The backbone angles of the chelating dppm ligands of 95.7(2)° (P1–C1–P2) and 94.7(2) ° (P3–C26–P4) lie in a typical region for iridium dppm complexes (see Table 1) while the backbone angle of the monodentate dppm of 117.0(3)° is much bigger than the value observed for uncoordinated dppm (106.2(3)°)[34] due to the increased steric pressure resulting from the attachment of the iridium substituent to P5.

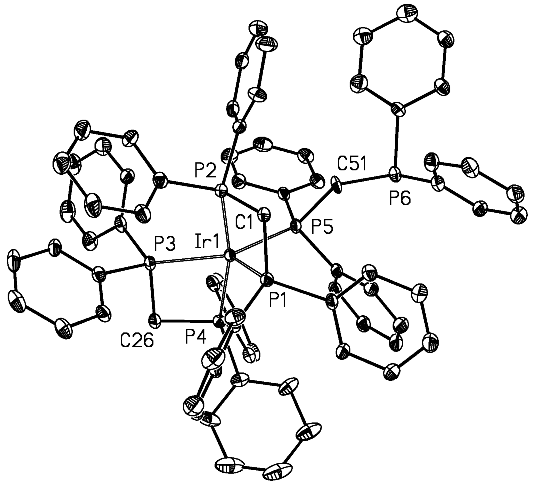
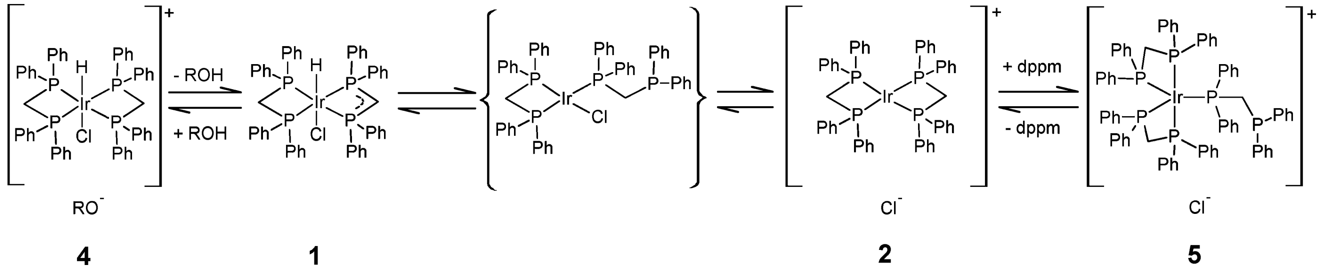


Fig. 3 Molecular structure of the cation of **5** (H-atoms and cocrystallized methanol are omitted for clarity). Selected distances (Å) and angles (°) are: Ir1–P1 2.3896(13), Ir1–P2 2.3153(13), Ir1–P3 2.2989(13), Ir1–P4 2.3327(13), Ir1–P5 2.3598(13), P1–Ir1–P2 71.18(4), P1–Ir1–P3 123.17(4), P1–Ir1–P4 109.25(4), P1–Ir1–P5 101.34(4), P2–Ir1–P3 95.91(5), P2–Ir1–P4 165.51(5), P2–Ir1–P5 97.99(5), P3–Ir1–P4 1.48(4), P3–Ir1–P5 135.48(5), P4–Ir1–P5 96.11(4), P1–C1–P2 95.7(2), P3–C26–P4 94.7(2), P5–C51–P6117.0 (3).

While such 18VE compounds of iridium(I) are rather common with electron withdrawing ligands like CO, the only other structurally characterized example of such a compound containing only phosphorus donors is [Ir(QP)(Ph$_3$P)][BPh$_4$] [QP = tris-(o-diphenylphosphinophenyl)phosphine] reported by Venanzi *et al.*[35] Complex **5** shows fluxional behaviour in methanol solution and only a very broad signal in the ^{31}P NMR spectra at $\delta = -57$ was observed at room temperature. At −50 °C this signal splits into three signals at $\delta = -13.4$, −24.4 and −64.1 with relative intensities of 1 to 1 to 4. Even at this temperature only broad signals were observed in the ^{1}H NMR spectra. Scheme 2 summarizes the compounds observed from the reaction of dppm with [Ir$_2$(μ-Cl)$_2$(coe)$_4$].

CO$_2$ activation by diphosphanylmethanide complexes

Among the isolated products and postulated intermediates (see Scheme 2), present in the equilibrium observed from the iridium mediated C–H activation of dppm, are several species with potential reaction sites for CO$_2$. It is known, that several iridium and rhodium complexes of the type [(L ∩ L)$_2$M]Cl with chelating phosphorus and arsenic ligands react with CO$_2$ forming metallacarboxylates of the type [(L ∩ L)$_2$MCl(CO$_2$)] [36,37] and one may expect that [Ir(dppm)$_2$]Cl, present in the above described equilibrium, is suitable for this reaction too. Furthermore, [IrCl(coe)(PMe$_3$)$_3$], [IrCl(PMe$_2$Ph)$_3$] and [Ir(PMe$_3$)$_4$]Cl are known to form an iridacycle by oxidative coupling of two CO$_2$ molecules.[38–40] A compound of the type [IrCl(PR$_3$)$_3$] can be assumed to be the reactive species in those cases and the proposed intermediate [IrCl(η^2-dppm)(η^1-dppm)][21] is expected to have a similar geometry at the iridium center and therefore maybe similar reactivity. When the reaction of [Ir$_2$(μ-Cl)$_2$(coe)$_4$] and dppm (1 to 4 ratio) was performed under a CO$_2$ atmosphere in various solvents (for instance toluene, thf, acetone or acetonitrile), a white precipitate rapidly formed. As preliminary reported, this compound was identified as [IrCl(dppm)(H){(Ph$_2$P)$_2$C–COOH}] (**6**).[19] The infrared spectrum of **6** shows strong broad bands at 1580 and 1270 cm^{-1}, while its insolubility in nearly all common



Scheme 2 Equilibria observed in the reaction of dppm with $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$

solvents prevents further investigations in solution by NMR. The identity of **6** was undoubtfully established by elemental analysis in combination with a X-ray diffraction study of crystals of **6**, obtained directly from the reaction mixture in acetone. Similar results were obtained when crude $[Ir_2(\mu\text{-}I)_2(coe)_4]$ prepared in analogy to a known procedure[41] was used. In this case, the corresponding iodo compound $[IrI(dppm)(H)\{(Ph_2P)_2C\text{–}COOH\}]$ (**7**) was isolated in good yields. The presence of the iodide ligand in **7** results in a shift of the hydride band to 2165 cm^{-1} due to its differing *trans* influence when compared to **6** (2185 cm^{-1}). Fig. 4 shows the molecular structure of **7**. Like the isostructural **6**, compound **7** crystallizes in the space group $P\bar{1}$. The iridium centre is surrounded by four phosphorus atoms, a hydride and a iodide ligand in a slightly distorted octahedral environment. In the formed anionic $(Ph_2P)_2C\text{–}COOH$ ligand the carbon atoms, C1 and C2 clearly exhibit sp^2 hybridizations (bond angles around C1 and C2 summing up to 359.3 and 360.0 and the P–C1 bonds (average 1.774(10) Å) are significantly shorter than in the standard coordinated dppm (av. 1.847(3) Å), consistent with a P–C partially multiple bond character and with the delocalization of the negative charge in the P1–C1–P2 fragment. However, these P–C distances are significantly longer then in the diphosphanylmethanide ligand in **1**. The carboxylic acid group is nearly coplanar with the P1–C1–P2 fragment forming a dihedral angle of 9.18°, very similar to that observed in the neutral carbodiphosphorane CO_2 adduct $(Ph_3P)_2C\text{–}CO_2$ (10.0°).[42] Like other carboxylic acids, **6** and **7** form dimers in the solid state through a double hydrogen bond (O1–O2′ 2.606 Å). As mentioned above the compounds **6** and **7** are closely related to carbodiphosphorane CO_2 and CS_2 adducts and should be treated as their metal containing counterparts. Table 2 summarizes some of the structural features of these adducts together with those of **6** and **7**. Although the C1–C2 bond in the carbodiphosphorane adducts is quite short, calculations have shown that the contribution of attractive π-orbital interactions to this bond is rather small.[42] The even shorter C1–C2 bond (see Table 2) in the iridium complexes **6** and **7** may indicate a higher degree of a multiple bond character and higher contribution of the resonance structure B (see Scheme 3) to the real bonding situation.

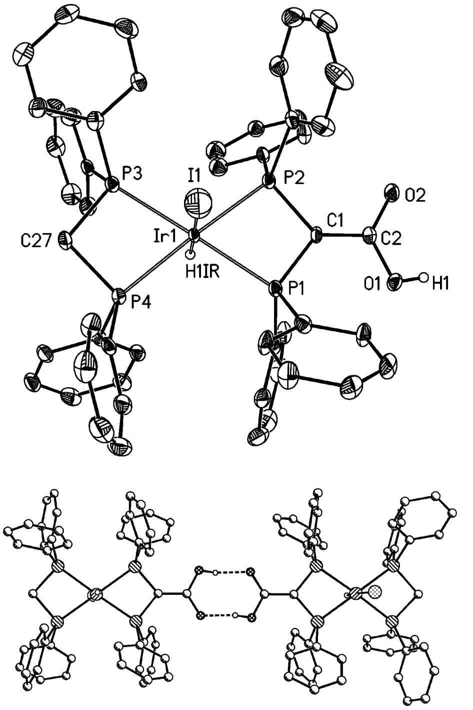
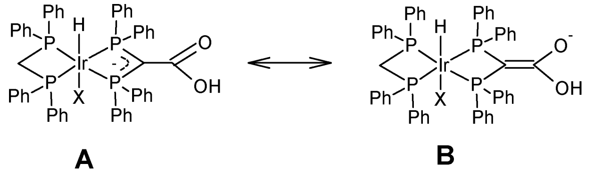


Fig. 4 Molecular structure of **7** (top) and dimeric unit (bottom), (most of the H-atoms and co-crystallized acetone are omitted for clarity; disorder of a phenyl ring is not shown). Selected distances (Å) and angles (°) are: Ir1–P1 2.343(2), Ir1–P2 2.363(2), Ir1–P3 2.344(2), Ir1–P4 2.334(2), Ir1–I 2.7369(10), P1–C1 1.771(10), P2–C1 1.776(9), P3–C27 1.853(10), P4–C26 1.844(10), C1–C2 1.407(14), C2–O1 1.323(11), C2–O2 1.274(11), P1–Ir1–P3 176.42(7), P2–Ir1–P4 172.00(8), P1–C1–P2 99.9(5), P3–C27–P4 96.03(5), O1–C2–O2 119.8(9).



Scheme 3 Mesomeric forms of **6** and **7**.

The observed structure of the newly formed ligand is in contrast to the lithium salt which arises from the reaction of $[Li(dppm\text{-}H)]_n$ with CO_2. In this case, the formation of a bis(diphenylphosphino)acetate ligand was reported but further analytical data was not available.[25] Therefore, the formation of $[Li\{(Ph_2P)_2CHCOO\}]$ was reinvestigated and recrystallization from dme was found to produce suitable crystals of the dinuclear complex $[Li(dme)\{(Ph_2P)_2CHCOO\}]_2$ (**8**) for X-ray diffraction experiments. The same compound was formed when a solution of the above mentioned lithium complex **3** was exposed to a CO_2 atmosphere. The molecular structure of **8** (molecule A of two independent molecules) shown in Fig. 5 illustrates, that in this complex indeed the other tautomeric form of the ligand known from the iridium complexes is observed. As expected, the geometries of those two ligands are quite different (see

Table 2 Selected bond lengths and angles of the complexes **6**, **7**, **8** and of related carbodiphosphorane adducts

	Distances (av.) [Å]			Angles (av.) [°]				
Compound	P–C	C–C	C–O (or S)	P–C–P	P–C–C	C–C–O (or S)	O–C–O (or S)	Reference
[$(Ph_3P)_2C–CO_2$]	1.721	1.494	1.259	135.2	112.2	116.2	127.7	42
[$(Ph_3P)_2C–CS_2$]	1.751	1.469	1.691	127.3	116.4	117.6	124.8	42
6	1.764	1.421	1.296	100.2	129.6	119.9	120.2	19
7	1.761	1.428	1.298	100.8	129.3	119.9	120.1	—
8	1.871	1.534	1.249	104.9	112.7	116.8	126.5	—

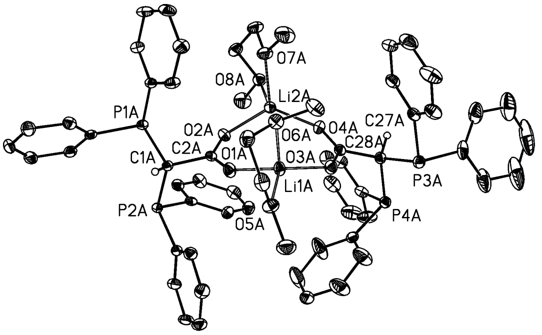


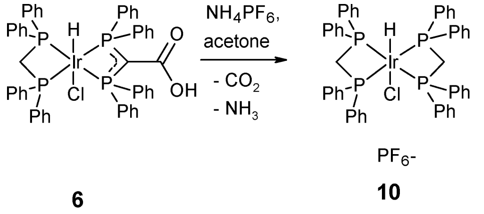
Fig. 5 Molecular structure of **8** (carbon atoms of dme and most of the H-atoms are omitted for clarity). Selected distances (Å) and angles (°) are: Li1A–O1A 1.867(6), Li1A–O3A 1.894(6), Li1A–O5A 2.052(6), Li1A–O6A 2.068(6), O1A–C2A 1.256(4), O2A–C2A 1.240(4), C1A–C2A 1.533(4), P1A–C1A 1.871(3), P2A–C1A 1.870(3). O1A–Li1A–O3A 129.5(3), O1A–Li–O5A 102.1(3), O1A–Li1A–O6A 105.7(3), O1A–C2A–O2A 126.6(3), O1A–C2A–C1A 116.8(3), O2A–C2A–C1A 116.5(3), P1A–C1A–P2A 104.77(16), P1A–C1A–C2A 109.3(2), P2A–C1A–C2A 114.8(2).

Table 2) and the ligand observed in the lithium salt truly is a bis(diphenylphosphino)acetate. NMR measurements of **8** in d_8-thf confirm, that the same tautomeric form of the ligand is observed in solution as well. Besides the signals of the dme ligand and the phenyl groups a triplet at $\delta = 4.11$ in the ^1H NMR spectrum and a triplet at $\delta = 48.2$ in the ^{13}C NMR spectrum were observed for the PCHP group. Additionally, the signal of the carboxylate function was found at $\delta = 174.8$ in the ^{13}C NMR spectrum.

The formation of the iridium complexes **6** and **7** can be explained by the initial C–H bond activation of dppm in the complex **2** leading to intermediate **1** or its iodo analog. As shown in Scheme 2, a coordinating anion is necessary for this reaction. Therefore the related compound [$Ir(dppm)_2$]PF_6 (**9**) containing the weakly coordinating PF_6^- anion was prepared in analogy to the known trifluoroacetate derivative.[30] Its composition was established by NMR measurement. In solution no C–H activation of coordinated dppm of **9** was observed and no reactivity towards CO_2 was found as well under the employed conditions.

The next steps in the formation of **6** and **7** are the nucleophilic attack of CO_2 by the methanide carbon followed by a proton shift to the formed carboxylate function resulting in formal insertion of CO_2 into the C–H bond of the diphosphanyl methanide anion. Ruiz *et al.* reported a similar insertion of alkynes into the C–H bond of a coordinated diphosphanyl methanide ligand in *fac*-[$Mn(CNtBu)(CO)_3\{(PPh_2)_2C–H\}$].[43] The low solubility of **6** and **7** in common organic solvents prevents their further investigation in solution. Chlorinated solvents slowly dissolve and react with **6** within days under release of CO_2. While the cation [$IrCl(dppm)_2(H)$]$^+$ was the only phosphorus containing species detected in dichloromethane, a untraceable mixture of products was formed in chloroform. The products formed may stem from the reaction of **6** with HCl slowly formed in those chlorinated solvents. A similar reactivity towards other acidic compounds like NH_4PF_6 supports this hypothesis.

This reaction leads to the formation of [$IrCl(dppm)_2(H)$]PF_6 (**10**) (see Scheme 4) which was identified an basis of its NMR spectra. Carbodiphosphorane CO_2 adducts react in a comparable way with acids underlining the similarity of **6** and **7** to those compounds.[44] Crystals of **10** obtained from acetone, acetonitrile or ethanol suffer from twining and were not suitable for X-ray diffraction experiments.



Scheme 4 Acid induced decarboxylation of **6.**

However, the related compound [$IrCl(dppm)_2(H)$]I (**11**) containing the same cation as **4** and **10** was obtained as side product of the reaction of [$Ir_2(\mu\text{-}I)_2(coe)_4$], dppm and CO_2 in toluene. **11** arises from impurities of the used starting material. The molecular structure of **11** is shown in Fig. 6.

In compound **11** the iridium atom has the same donor set consisting of four phosphorus atoms, a hydride and a chloride as the one in compound **1**. The distances and angles of the coordinated dppm ligands in those complexes are similar. As expected the main difference is the shorter Ir1–Cl bond of 2.467(3) Å in the cation of **11** when compared to the Ir1–Cl bond of 2.513(2) Å in neutral **1**.

Finally, it should be mentioned that no insertion of CO_2 into the Ir–H bonds of the reported complexes was observed under the applied conditions (room temperature, CO_2 pressure up to 0.4 bar).

Conclusions

The reaction between dppm and [$IrX(coe)_2$]$_2$ results in the formation of various products partially connected which each other *via* different equilibria. The variation of the solvent and the ligand to metal ratio allows the isolation of some of those products (**1**, **2**, **5**; X = Cl). When such a reaction mixture is

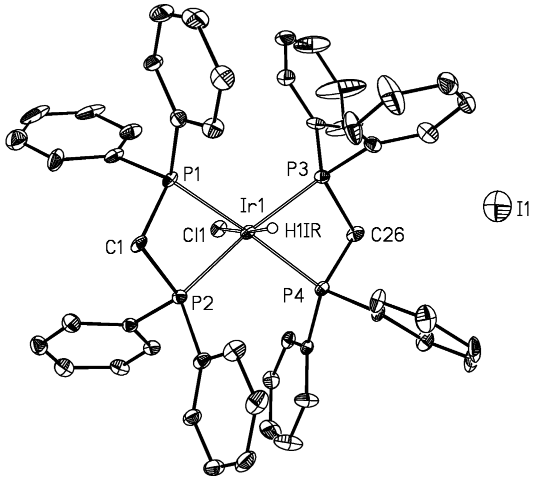


Fig. 6 Molecular structure of **11** (most of the H-atoms are omitted for clarity). Selected distances (Å) and angles (°) are: Ir1–P1 2.342(3), Ir1–P2 2.311(3), Ir1–P3 2.349(3), Ir1–P4 2.316(3), Ir1–Cl 2.467(3), P1–C1 1.861(13), P2–C1 1.823(11), P3–C26 1.833(11), P4–C26 1.848(12), P1–Ir1–P4 171.65(10), P2–Ir1–P3 173.35(10), P1–C1–P2 95.1(5), P3–C26–P4 94.2(5).

exposed to a CO_2 atmosphere, the surprisingly selective formation of $[IrX(dppm)(H)\{(Ph_2P)_2C\text{–}COOH\}]$ (**6**: X = Cl, **7**: X = I) was observed containing an unique anionic ligand. This ligand is most likely formed from dppm by a C–H activation/CO_2 carboxylation sequence mediated by iridium. Comparison with related lithium compounds indicates that the iridium center with its strong preference for the phosphorus donors of the ligand is responsible for its tautomerisation while in case of lithium the expected diphosphinoacetate ligand was observed.

The observed tautomer in **6** and **7** shows some remarkable similarities with carbodiphosphorane-CO_2 adducts making complexes with this ligand an interesting subject for further studies if derivatives with higher solubility can be found.

Experimental

General data

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were dried according to common procedures and distilled under argon, deuterated solvents were dried over sodium, degassed, and saturated with argon. Acetone was dried with $CaCl_2$ and distilled before used. $[Ir_2(\mu\text{-}X)_2(coe)_4]$ was prepared according (X = Cl) [45] or in analogy (X = I) to literature methods.[41] Crude impure $[Ir_2(\mu\text{-}I)_2(coe)_4]$ obtained this way was used without further purification. Dppm was purchased from Aldrich. CO_2 (99.999%) was purchased from Air Liquide and used without further purification. The ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker AC 400 MHz or 200 MHz spectrometer. Chemical shifts are reported in parts per million and referenced to $SiMe_4$ using the residual signal of the deuterated solvent as reference and 85% phosphoric acid, respectively. Infrared spectra were recorded using a Perkin–Elmer Spectrum One spectrometer. Carbon and hydrogen analyses were performed with a Perkin–Elmer 2400 microanalyzer.

Synthesis of [Ir(dppm)]Cl (2) and formation of $[IrCl(dppm)_2(H)][OR]$ (4a: R = Et; 4b: R = Me)

Ethanol (8 ml) was added to a mixture of solid $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ (67 mg, 0.075 mmol) and dppm (115 mg, 0.299 mmol). The obtained suspension was stirred until all solids were dissolved resulting in a red solution. This solution was stored at −20 °C over night. Afterwards the volume was reduced in a vacuum to approximately 2 ml until crystallization of a red compound started. Then the stirring was stopped and the solution was allowed to stand 1 h at room temperature resulting in the formation of red crystals of **2**. The mother liquor was decanted and the residue was rapidly washed with 2 ml of a mixture of thf and ethanol (2 to 1) and dried *in vacuo*. The crystals partially lose cocrystallized ethanol on drying. Yield: 85 mg. δ_P(81.0 MHz, d_8-THF–EtOH): −35.7 (s, **2**), −53.9 (s, **4a**).

A sample of red **2** was dissolved im d_4-Methanol. The obtained pale yellow solution contained $[IrCl(d_2\text{-}dppm)_2(H)][OCD_3]$ (**4b**) as sole iridium containing product. δ_H(200 MHz, d_4-MeOH): −16.45 (1H, quint., $^2J_{H,P}$ 12.0, Ir–H), 1.17 (~6H, t, $^3J_{H,H}$ 7.0, CH_3 EtOH), 3.60 (~4H, q, $^3J_{H,H}$ 7.0, CH_2 EtOH), 7.2–7.6 (40 H, m, CH Ph). δ_P(81.0 MHz, d_4-MeOH): −53.9 (s).

Synthesis of $[Li(dme)_2(dppm\text{-}H)]$ (3)

$[Li(dppm\text{-}H)]_n$[25] (0.52 g, 1.33 mmol) was dissolved in dme (20 ml), stirred for 30 min and evaporated to dryness. The pale yellow residue was washed with cold diethyl ether (2 × 5 ml) and dried in a vacuum. Yield 0.59 g (78%). Found: C, 69.0; H, 7.2% $C_{33}H_{41}LiO_4P_2$ requires C, 69.5; H, 7.2%. δ_H(400 MHz, d_8-THF) 1.61 (1H, t, $^2J_{H,P}$ 8.4, CH), 3.27 (12H, s, CH_3 dme), 3.44 (8H, s, CH_2 dme), 6.97 (4H, m, *p*-CH Ph), 7.08 (8H, m, *m*-CH Ph), 7.56 (8H, m, *o*-CH Ph). δ_C(50.3 MHz, d_8-THF) 18.5 (1C, t, $^1J_{C,P}$ 17.8, P_2CH), 58.8 (4C, s, CH_3 dme), 72.6 (4C, s, CH_2 dme), 125.4 (4C, s, *p*-CH Ph), 127.3 (8C, t, *J* 2.8, *m*-CH-Ph), 132.0 (8C, t, *J* 7.9, *o*-CH Ph), 152.5 (4C, t, *J* 3.4, *i*-C Ph). δ_P(81.0 MHz, d_8-THF) 3.1(s). Suitable crystals for X-ray measurement were obtained by cooling a saturated solution of **3** in dme from room temperature to −20 °C.

Synthesis of $[Ir(\eta^1\text{-}dppm)(\eta^2\text{-}dppm)_2]Cl{*}6CH_3OH$ (5)

Dppm (70 mg, 0.182 mmol) was added to a suspension of $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ (25 mg, 0.028 mmol) in methanol (6 ml) and the resulting mixture was stirred for 4h. Afterwards the solution was filtered and concentrated to 2 ml in a vacuum. Storage at −40 °C resulted in formation of yellow orange crystals within a week. The supernatant solution was decanted and the residue was dried in a vacuum. The compound loses the cocrystallized methanol on prolonged drying *in vacuo*. Yield 63 mg (85%). Found: C, 65.0; H, 4.8% $C_{75}H_{66}IrClP_4$ requires C, 65.2; H, 4.8%; δ_P(81.0 MHz, d_8-THF, 223 K) −13.4 (1P, q, $^2J_{P,P}$ 29.3), −24.4 (1P, d, $^2J_{P,P}$ 29.5), −64.1 (4P, d, $^2J_{P,P}$ 29.2).

Synthesis of $[IrCl(dppm)(H)\{(Ph_2P)_2C\text{–}COOH\}]$ (6)

Dppm (102 mg, 0.27 mmol) in toluene (5 ml) was added to a stirred suspension of $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ (56 mg, 0.062 mmol) in toluene (5 ml). The initially red solution bleached to yellow and the argon atmosphere was replaced by CO_2 resulting in further bleaching to pale yellow and precipitation of a colourless solid. The reaction mixture was stirred for additional three hours. Afterwards the supernatant solution was decanted and the remaining white residue was washed with toluene (2 × 5 ml) and diethyl ether (2 × 5 ml). The obtained product **6**·0.5toluene was dried in a vacuum. Yield 131 mg (96%). Found: C, 60.3; H, 4.5% $C_{54.5}H_{48}IrClO_2P_4$ requires C, 60.25; H, 4.45%. ν_{max}/cm^{-1} 2185w (Ir–H), 1580br (COO), 1270br (COO).

Similar results were obtained in thf, acetone or acetonitrile. **6** is insoluble in common organic solvents like toluene, diethyl ether, thf or acetone, and dissolves slowly and decomposes in chlorinated solvents like $CHCl_3$ and CH_2Cl_2.

Suitable crystals of the composition **6**·3acetone for X-ray measurement were obtained directly from a reaction mixture in acetone.

Synthesis of [IrI(dppm)(H){(Ph$_2$P)$_2$C–COOH}] (7)

A solution of dppm (72 mg, 0.19 mmol) in thf (4 ml) was added to a stirred suspension of $[Ir_2(\mu\text{-}I)_2(coe)_4]$ (51 mg, 0.047 mmol) in thf (5 ml). The resulting brown solution was pressured with CO_2 (0.2 bar) and was allowed to stand overnight. Afterwards the supernatant solution was decanted from the formed microcrystalline solid. The residue was washed with diethyl ether (2 × 5 ml) and dried in a vacuum. Yield 85.5 mg (80%). ν_{max}/cm^{-1} 2165w (Ir–H), 1590br (COO), 1265br (COO).

Similar results were obtained in toluene or acetone. Suitable crystals of the composition **7**·3acetone for X-ray measurement were obtained directly from a reaction mixture in acetone. Suitable crystals of compound **11** for X-ray measurement were obtained as an impurity from the mother liquor of the reaction in toluene.

Synthesis of [Li$_2${OOC–CH(PPh$_2$)$_2$}$_2$(dme)$_2$] (8)

[Li{OOC–CH(PPh$_2$)$_2$}][25] was recrystallized from dimethoxyethane. **8** was obtained as colourless crystals.

δ_H(400 MHz, d$_8$-THF) 3.28 (12H, s, CH_3 dme), 3.44 (8H, s, CH_2 dme), 4.11 (2H, t, $^2J_{H,P}$ 2.8, CH), 7.03–7.13 (24H, m, CH Phenyl), 7.41–7.48 (8H, m, CH Ph), 7.52–7.59 (8H, m, CH Ph); δ_C(50.3 MHz, d$_8$-THF) 48.2 (2C, t, $^1J_{C,P}$ 25.7, P_2CH), 58.8 (4C, s, CH_3 dme), 72.6 (4C, s, CH_2 dme), 128.0–128.4 (12C, m, CH Ph), 134.3 (4C, t, *J* 10.8, *o*-CH–Ph), 135.2 (4C, t, *J* 11.4 Hz, *o*-CH Ph), 140.1 (2C, t, *J* 5.7, *i*-C Ph), 140.9 (2C, t, *J* 4.8, *i*-C Ph), 174.8 (2C, s, COO); δ_P(81.0 MHz, d$_8$-THF) –9.8 (s). ν_{max}/cm^{-1} 1625 (COO).

Synthesis of [Ir(dppm)$_2$]PF$_6$ (9)

$[Ir(dppm)_2]PF_6$ was prepared in analogy to [Ir(dppm)$_2$]OTf.[30]

δ_H(400 MHz, d$_6$-acetone) 5.22 (4H, br, PCH_2P), 7.3–7.6 (40H, m, Ph); δ_P(162.0 MHz, d$_6$-acetone) −35.7 (4P, s, dppm), −144.0 (1P, sept, $^1J_{P,F}$ 711, PF_6).

Synthesis of [IrCl(dppm)$_2$(H)]PF$_6$ (10)

NH_4PF_6 (14.7 mg, 0.09 mmol) was added to a stirred suspension of **6** (77.2 mg, 0.074 mmol) in acetone (5 ml). Within 1 h a clear colourless solution formed and the solvent was removed in a vacuum. The remaining solid was washed with diethyl ether (3 × 4 ml) and dried in a vacuum. Yield: 85 mg (crude product, contains the excess of NH_4PF_6). As judged from the ^{31}P nmr, **10** is the only dppm containing product formed. A sample recrystallized from acetone was used for elemental analysis. Found: C, 52.7; H, 4.0%

Table 3 Crystal data and refinement details for the X-ray structure determinations

Compound	**1**	**3**	**5**	**7**	**8**	**11**
Formula	$C_{50}H_{44}ClIrP_4$ $0.5\cdot(C_4H_{10}O_2)$	$C_{33}H_{41}LiO_4P_2$	$[C_{75}H_{66}IrP_6]^+$ Cl^- $6\cdot(CH_4O)$	$C_{51}H_{44}IIrO_2P_4$ $3\cdot(C_3H_6O)$	$C_{60}H_{62}Li_2O_8P_4$	$[C_{50}H_{45}ClIr\ P_4]^+$ I^-
fw/g mol^{-1}	1041.44	570.54	1573.00	1306.16	1048.86	1124.29
T/° C	–90(2)	–90(2)	–90(2)	–173(2)	–90(2)	–90(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	9.9857(3)	16.2326(6)	20.9095(3)	12.3388(7)	11.5057(2)	12.7210(5)
b/Å	21.0322(6)	9.2525(2)	13.8595(2)	13.1005(7)	15.9886(4)	16.1700(3)
c/Å	21.3775(7)	21.7101(7)	27.8469(5)	17.6742(10)	32.4517(6)	25.2040(7)
α (°)	90	90	90	84.285(2)	92.367(1)	90
β (°)	94.868(2)	106.354(2)	111.662(1)	79.868(2)	90.741(1)	120.220(3)
γ (°)	90	90	90	79.862(2)	110.614(1)	90
V/Å^3	4473.5(2)	3128.76(17)	7500.0(2)	2761.5(3)	5580.4(2)	4479.9(2)
Z	4	4	4	2	4	4
ρ/g cm^{-3}	1.546	1.211	1.393	1.571	1.248	1.667
μ/mm^{-1}	32.26	1.74	19.96	31.4	1.89	39.06
measured data	30048	10804	49853	25015	31591	41253
data with $I > 2\sigma(I)$	6285	2844	11474	8418	15912	7899
unique data (R_{int})	10210/0.1292	3572/0.0384	17055/0.0942	9747/0.0766	23791/0.0341	10225/0.0910
wR_2 (all data, on F^2)^a	0.1268	0.1037	0.1232	0.1739	0.2019	0.2321
R_1 ($I > 2\sigma(I)$)^a	0.0603	0.0359	0.0524	0.0606	0.0769	0.0833
s^b	1.007	1.015	1.033	1.018	1.009	1.031
Res. dens./e Å^{-3}	1.975/–1.039	0.263/–0.239	1.762/–0.896	2.263/–4.982	0.881/–0.781	1.614/–1.599
absorpt method	NONE	NONE	NONE	empirical	NONE	NONE
CCDC No.	770462	770463	770464	770465	770466	770467

[a] Definition of the *R* indices: $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$. [b] $s = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

$C_{50}H_{45}IrClF_6P_5$ requires C, 52.6; H, 4.0%. ν_{max}/cm^{-1} 2198w (Ir–H). δ_H(400 MHz, CD_2Cl_2) −16.39 (1H, quint., $^2J_{H,P}$ 12.1, Ir–H), 5.1–5.25 (2H, m, C*H*H'), 5.30–5.45 (2H, m, CH*H'*), 7.1–7.25 (32H, m, CH Ph), 7.35–7.45 (8H, m, CH Ph); δ_C(75 MHz, CD_2Cl_2) 50.1 (2C, quint., $^1J_{C,P}$ 15.6, P–CH_2–P), 128.0 (4C, quint., *J* 15.5, *i*-C Ph), 129.0 (8C, quint., *J* 2.6, CH Ph), 129.5 (8C, quint., *J* 2.6, CH Ph), 131.2 (4C, quint., *J* 15.2, *i*-C Ph), 132.1 (4C, s, *p*-CH Ph), 132.5 (4C, s, *p*-CH Ph), 133.0 (8C, quint., *J* 3.2, CH Ph), 133.4 (8C, quint., *J* 2.9, CH Ph). δ_P(121.5 MHz, CD_2Cl_2) −55.2 (4P, s, dppm), −144.2 (1P, sept., $^1J_{P,F}$ 711.3, PF_6).

A related complex [IrCl(dppm)$_2$(H)]BF_4 has been previously reported.[21]

Crystal structure determinations

The intensity data for the compounds **1**, **3**, **5**, **8** and **11** were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were corrected for Lorentz and polarization effects but not for absorption effects.[46,47] The structures were solved by direct methods (SHELXS)[48] and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97) (Table 3).[49] All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-disordered non-hydrogen atoms were refined anisotropically. The intensity data for **7** was recorded at 100(2) K on a Bruker-AXS Smart CCD diffractometer, using a ω scan technique with Mo-Kα radiation. The structure was solved by direct methods (SHELXS-97)[48] and refined on F^2 by full-matrix least-squares techniques using the SHELXL-97 program.[49] Non-hydrogen atoms were refined with anisotropic displacement parameters, and most hydrogen atoms were refined from observed positions. The hydride ligand was included from electrostatic potential calculations (HYDEX program).[50] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Acknowledgements

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