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A C–H activation–CO_2-carboxylation reaction sequence mediated by an 'Iridium(dppm)' species. Formation of the anionic ligand $(Ph_2P)_2C$–COOH†

Jens Langer,*‡ María José Fabra, Pilar García-Orduña, Fernando J. Lahoz and Luis A. Oro*

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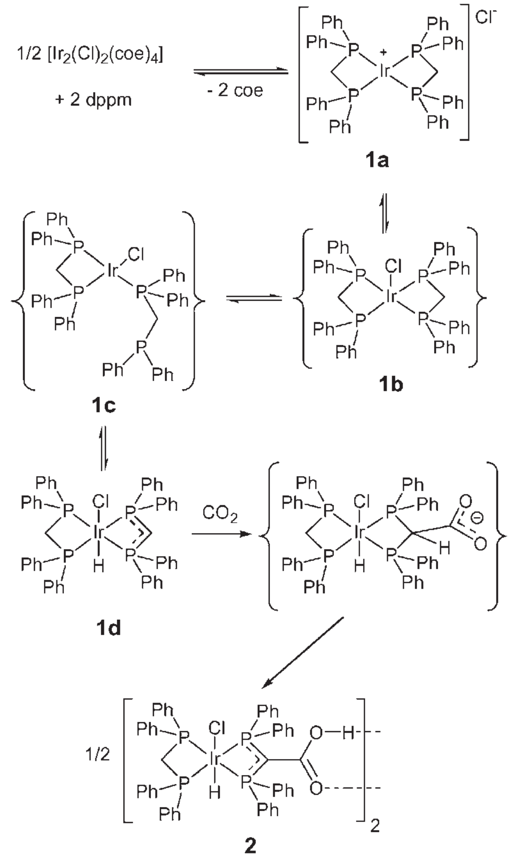
The reaction of $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ with 1,1-bisdiphenylphosphinomethane under CO_2 atmosphere affords the complex $[IrCl(dppm)(H)\{(Ph_2P)_2C\text{–}COOH\}]_2$ by initial CH activation followed by formal insertion of CO_2 into the C–H bond of the formed diphosphanylmethanide ligand.

The activation of small molecules like CO_2 and the modification of alkanes by C–H activation are among the goals of modern organometallic and coordination chemistry. Although in both fields significant progress has been reported during the last decades,[1,2] there are still only a few examples of transition metal complexes, which are able to selectively functionalize alkanes by a C–H activation–CO_2 carboxylation sequence.[1] Initial investigations by Herskovitz showed that iridium compounds can be used to carboxylate acetonitrile,[3] but the products were not isolated. Later Behr *et al.* demonstrated, that the use of the more acidic malonodinitrile (pK_a = 12) made possible the isolation of the products and their complete characterization. They were able to determine the X-ray structures of $[IrCl(depe)_2(H)]^+[HOOCC(CN)_2]^-$ and $[Ir(H)_2(PMe_3)_4]^+[HOOCC(CN)_2]^-$.[4]

We herein report the iridium mediated transformation of the less acidic dppm (1,1-bisdiphenylphosphinomethane, pK_a = 29.9[5]) into an unpredicted anionic ligand *via* a C–H activation–carboxylation sequence.

The system dppm–$[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ (coe = cyclooctene) was chosen as a promising candidate for CO_2 activation due to the fluxional behavior of the resulting product "$dppm_2IrCl$" in solution as reported by Tejel *et al.*[6] The products and intermediates **1a–1d** (see Scheme 1) are species with potential reaction sites for CO_2. The iridium(I) complex $[Ir(dppm)_2]Cl$ is similar to complexes of the composition $[IrL_4]Cl$ (L_2 = dmpe or L = PMe_3) which react with CO_2 either to form metallacarboxylates[7] or to oxidatively couple two CO_2 molecules.[8]



Scheme 1 Proposed mechanism for the formation of **2**.

Interestingly, the reaction of $[Ir_2(\mu\text{-}Cl)_2(coe)_4]$ with dppm (1 : 4 ratio) under a CO_2 atmosphere in various solvents (for instance toluene, thf, acetone or acetonitrile) leads to the formation of a white product **2** within minutes. IR measurements show strong bands at 1580 and 1270 cm^{-1} which were not observed in absence of CO_2. Although similar to those reported for the metallacarboxylate $[IrCl(CO_2)(dmpe)_2]$ (1550 and 1230 cm^{-1}), the obtained product shows different reactivity.[7] For instance, no reaction was observed with methyl triflate in toluene suspension.

An X-ray diffraction study§ of crystals of **2**, obtained from acetone, shows that the unexpected carboxylation of a dppm

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Departamento de Química Inorgánica, Instituto Universitario de Catálisis Homogénea, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009-Zaragoza, Spain. E-mail: oro@unizar.es; j.langer@uni-jena.de; Fax: +34 976 761143; Tel: +34 976 761143

† Electronic supplementary information (ESI) available: Full experimental details and analytical data for **2** and **3**. NMR data for $[Li\{OOCCH(Ph_2P)_2\}(tmeda)]$, $[Ir(dppm)_2]PF_6$ and $[Ir(dcypm)_2]Cl$. CCDC reference numbers 689715 (**1d**) and 689716 (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b809331h

‡ Current address: Institut für Anorganische und Analytische Chemie, FSU Jena, August-Bebel-Straße 2, 07743 Jena, Germany.

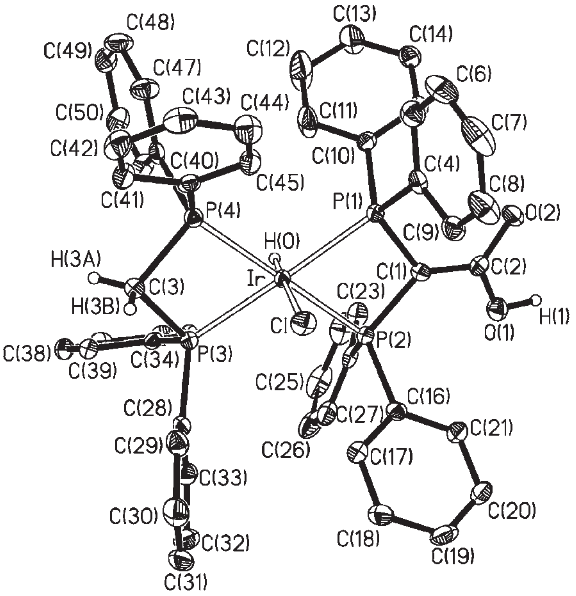


Fig. 1 Molecular structure of **2**. (Most of H atoms have been omitted for clarity). Selected distances (Å) and angles (°) are: Ir–P(1) 2.3463(9), Ir–P(2) 2.3340(9), Ir–P(3) 2.3206(9), Ir–P(4) 2.3405(9), Ir–Cl 2.4806(9), P(1)–C(1) 1.763(4), P(2)–C(1) 1.764(4), P(1)/P(2)–C(Ph) 1.822(2), P(3)–C(3) 1.840(4), P(4)–C(3) 1.853(4), P(3)/P(4)–C(Ph) 1.819(2), C(1)–C(2) 1.421(5), C(2)–O(1) 1.296(4), C(2)–O(2) 1.295(4); P(1)–Ir–P(3) 172.25(3), P(2)–Ir–P(4) 177.22(3), Cl–Ir–H(0) 175.5(15), P(1)–C(1)–P(2) 100.17(18), P(1)–C(1)–C(2) 129.1(3), P(2)–C(1)–C(2) 130.0(3), P(3)–C(3)–P(4) 95.65(17).

ligand has taken place. Compound **2** (Scheme 1) crystallizes in the space group $P\bar{1}$ and it shows the iridium centre surrounded by four phosphorus atoms, a hydride and a chloride ligand in a slightly distorted octahedral environment (Fig. 1). Compared to **1d** (see Fig. 2) the coordination sphere of the iridium atom has not changed too much and similar distances and angles around the metal were observed. In the formed anionic $(Ph_2P)_2C$–COOH ligand the carbon atoms, C(1) and C(2), clearly exhibit sp^2 hybridizations (bond angles around C(1) and C(2) summing up 359.27 and 360.0°) and the P–C(1) bonds (average 1.764(3) 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 P(1)–C(1)–P(2) fragment.

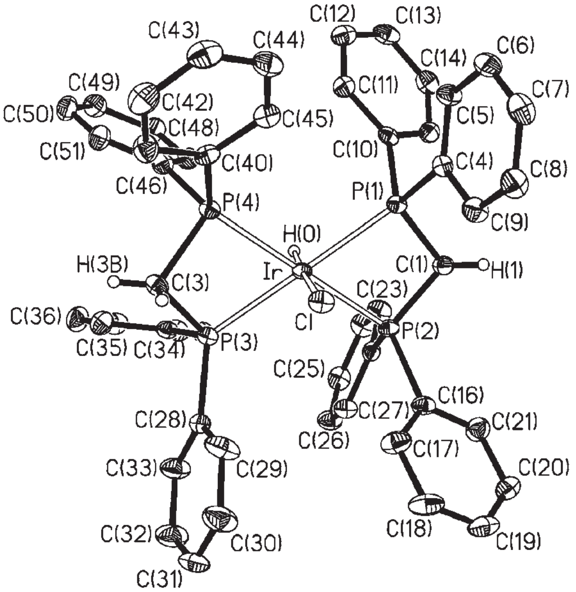


Fig. 2 Molecular structure of **1d**. Selected distances (Å) and angles (°) are: Ir–P(1) 2.3534(8), Ir–P(2) 2.3390(8), Ir–P(3) 2.3258(8), Ir–P(4) 2.3277(8), Ir–Cl 2.4945(8), P(1)–C(1) 1.726(3), P(2)–C(1) 1.723(3), P(1)/P(2)–C(Ph) 1.832(2), P(3)–C(3) 1.843(3), P(4)–C(3) 1.847(3), P(3)/P(4)–C(Ph) 1.819(2); P(1)–Ir–P(3) 173.62(3), P(2)–Ir–P(4) 176.24(3), Cl–Ir–H(0) 176.1(17), P(1)–C(1)–P(2) 100.47(18).

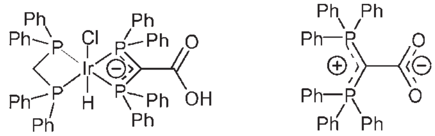
The carboxylic acid group is nearly coplanar with the P(1)–C(1)–P(2) fragment forming a dihedral angle of 8.14(10)°, very similar to that observed in the neutral carbodiphosphorane CO_2 adduct $(Ph_3P)_2C$–CO_2 (10.0°).[9] Like other carboxylic acids, **2** forms dimers in the solid state through a double hydrogen bond (O(1)–O(2)′ 2.600(4) Å), which makes both C(2)–O bond distances identical. In contrast, the corresponding lithium salt was described as a [bis(diphenylphosphino)acetate],[10] but neither infrared nor NMR data were reported. Therefore, the related base adduct with tmeda (*N*,*N*,*N*′*N*′-tetramethylethylendiamine) was prepared and NMR measurements support the description of the ligand as a [bis(diphenylphosphino)acetate] (see supporting information).

We propose the mechanism displayed in Scheme 1 to explain the formation of complex **2**. Initially, a C–H bond activation in the proposed square-planar complex **1c** afforded **1d**. Afterwards, a new C–C bond is formed by nucleophilic attack of the diphosphanylmethanide carbon to the carbon of CO_2, followed by proton migration. A similar insertion of alkynes into the C–H bond of a diphosphanylmethanide ligand in *fac*-[Mn(CN*t*Bu)$(CO)_3${$(PPh_2)_2$C–H}] was reported by Ruiz *et al.*[11] The structure of **1d**, determined by X-ray diffraction is shown in Fig. 2.

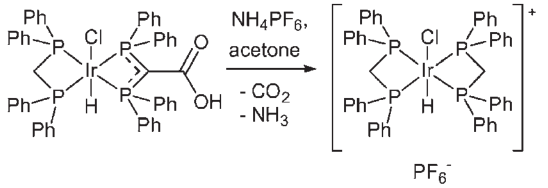
Like in related diphosphanylmethanide complexes,[12] the formed four membered ring Ir,P(1),C(1),P(2) is planar. The distances Ir–P(1) (2.3534(8) Å) and Ir–P(2) (2.3390(8) Å) are slightly longer than reported for [Ir(dppm-H)(H)(tp)] (tp = trispyrazolylborate) (2.276 and 2.269 Å),[13] but very similar to those observed in **2** (see Fig. 1). The major difference between **1d** and **2** concerns the P–C(1) bond distances in the methanide moieties, being remarkably longer in **2** (1.764(3) Å) than those observed in **1d** (1.725(3) Å), reflecting the different electronic properties of C(1) due to the presence of the carboxylic acid function in **2**.

The formation of **1d** as intermediate can be verified by blocking the C–H activation reaction. This has been done by exchanging the anion in the starting material, since a coordinating anion is necessary for the C–H activation to proceed *via* **1c** or by increasing the steric crowding around the iridium centre to prevent the attack of the chloride anion to form such an intermediate. Using a similar synthetic pathway to that used for the preparation of **1a**, complexes $[Ir(dppm)_2]PF_6$ and $[Ir(dcypm)_2]Cl$ (dcypm = 1,1-bisdicyclohexylphosphinomethane) were generated *in situ* and found to be stable in solution. C–H activation was not observed. Consequently, these compounds did not react with CO_2 under the applied conditions.

It is interesting to note, that the newly formed ligand does not act as a P,P,O scorpionate ligand Instead the remaining hydrogen of the former CH_2 group of dppm is transferred to



Scheme 2



2 **3**

Scheme 3 Acid induced decarboxylation of **2**.

the carboxylate function and the anionic PCP fragment is reformed. The similarity of the resulting compound to carbodiphosphorane CO_2 adducts of the type $[(R_3P)_2C–CO_2]$[9] is remarkable (see Scheme 2). **2** should be treated as their metalorganic analogue and is potentially useful as a carbene precursor like other carbene CO_2 adducts.[14]

The low solubility of **2** in common organic solvents prevents its further investigation in solution. Chlorinated solvents slowly dissolve and react with **2** within days under release of CO_2. While an untraceable mixture of products was formed in chloroform, the cation $[IrCl(dppm)_2(H)]^+$ was the only phosphorous containing species observed in dichloromethane. This species probably results from the attack of *in situ* formed HCl.

Therefore, the reactivity of **2** towards other acids and bases was also briefly examined. Reaction with NH_4PF_6 leads to $[IrCl(dppm)_2(H)]PF_6$ **3** (see Scheme 3) with complete loss of CO_2, underlining its similarity to carbodiphosphorane CO_2 adducts, which react in a comparable way.[15]

Attempts to remove the proton of the carboxylic acid function with neutral bases like triethylamine were unsuccessful even when the base was used in high excess. The use of an excess of anionic bases like KO*t*Bu was found to be more promising. Indeed, deprotonation of the acid function was achieved, as judged by infrared measurement, but it was complicated by the competing deprotonation of the second dppm ligand.

Other lithium and potassium bases are under current investigation to provide a clean access to the deprotonated form of **2**, which should be a valuable precursor for heterobimetallic compounds. Further studies to use **2** as CO_2 transfer reagent to C–H acid compounds like reported for N-heterocyclic carbene CO_2 adducts,[16] are also in progress.

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Notes and references

§ X-Ray diffraction data for **1d** and **2** were recorded at 100(2) K on a Bruker-AXS Smart CCD diffractometer, using a ω scan technique with Mo-Kα radiation (λ = 0.71073 Å). Both structures were solved by direct methods (SHELXS-97) and refined on F^2 by full-matrix least-squares techniques using the SHELXL-97 program. Non-hydrogen atoms were refined with anisotropic displacement parameters, and most hydrogen atoms were refined from observed positions. The hydride ligands were included from electrostatic potential calculations (HYDEX program).

Crystallographic data for complex **1d**: $C_{50}H_{44}ClIrP_4 \cdot 1.5C_7H_8$, M = 1134.58, triclinic, space group $P\bar{1}$, a = 10.6704(7), b = 11.7099(8), c = 20.3601(14) Å, α = 85.152(1), β = 76.129(1), γ = 88.756(1)°, V = 2461.0(3) Å^3, Z = 2, μ = 2.938 mm^{-1}, D_{calc} = 1.531 Mg m^{-3}, $F(000)$ = 1146, 30 715 reflections collected, 11 798 unique (R_{int} = 0.0309), $R1$ = 0.0328 ($F^2 > 2\sigma(F^2)$), $wR2$ = 0.0788 (all data) and GOF = 1.105. CCDC 689715.

Complex **2**: $C_{51}H_{44}ClIrO_2P_4 \cdot 3C_3H_6O$, M = 1214.63, triclinic, space group $P\bar{1}$, a = 12.3699(12), b = 13.1164(13), c = 17.4537(17) Å, α = 83.760(2), β = 79.883(2), γ = 79.480(2)°, V = 2732.3(5) Å^3, Z = 2, μ = 2.658 mm^{-1}, D_{calc} = 1.476 Mg m^{-3}, $F(000)$ = 1232, 32 782 reflections collected, 11 929 unique (R_{int} = 0.0437), $R1$ = 0.0348 ($F^2 > 2\sigma(F^2)$), $wR2$ = 0.0744 (all data) and GOF = 1.036. CCDC 689716.

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