C–C Coupling of Activated Alkanes with Carbon Dioxide by Iridium and Rhodium Complexes: Synthesis and Crystallographic Characterization of [H₂Ir(PMe₃)₄]⁺[O₂CCH(CN₂]−†

$$[H_2Ir(PMe_3)_4]^+[O_2CCH(CN_2]^-†$$

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HIr(PMe₃)₄ reacts with malonodinitrile and carbon dioxide to give [H₂Ir(PMe₃)₄]⁺[O₂CCH(CN)₂]−, the structure of which has been determined by X-ray diffraction.
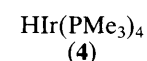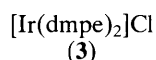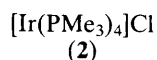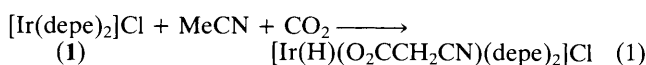
The activation of carbon–hydrogen bonds by transition metal complexes as a means of modifying alkanes has been of interest during the past two decades,[1] but only a few examples of metallation and subsequent carboxylation of activated hydrocarbons have been reported. Herskovitz et al. described the reaction of [Ir(depe)₂]Cl (1) (depe = Et₂PCH₂CH₂PEt₂) with acetonitrile and carbon dioxide [equation (1)].[2] The product was only characterized spectroscopically in solution. The related complexes [Ir(PMe₃)₄]Cl[2] (2), [Ir(dmpe)₂]Cl[3] (3), and (H)Fe(dmpe)₂(Np) (dmpe = Me₂PCH₂CH₂PMe₂; Np = 2-naphthyl)[4] appear to react in a similar way. We report the reaction of malonodinitrile with iridium and rhodium complexes under CO₂ pressure [equation (2)].

$$[Ir(depe)_2]Cl + MeCN + CO_2 \longrightarrow [Ir(H)(O_2CCH_2CN)(depe)_2]Cl \quad (1)$$
$$(1) \qquad\qquad\qquad [Ir(H)(O_2CCH_2CN)(depe)_2]Cl$$

[Ir(PMe₃)₄]Cl	[Ir(dmpe)₂]Cl
(2)	(3)

HIr(PMe₃)₃	[H₂Ir(PMe₃)₄]⁺[O₂CCH(CN)₂]−
(4)	(5)

[Rh(dmpe)₂]Cl	trans-[HM(L)₂Cl]⁺[O₂CCH(CN)₂]−
(6)	(7), M = Ir, L = depe
	(8), M = Rh, L = dmpe

$$[L_nMX] + CH_2(CN)_2 + CO_2 \longrightarrow [L_nMXH]^+[O_2CCH(CN)_2]^- \quad (2)$$

$$L = PMe_3 \ (n = 4), \ dmpe, \ or \ depe \ (n = 2)$$
$$X = Cl, H; M = Ir, Rh$$
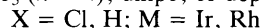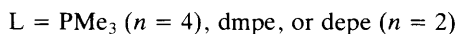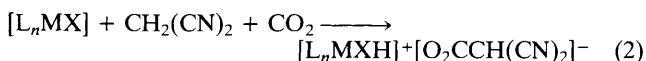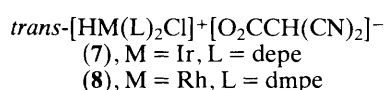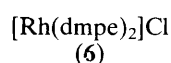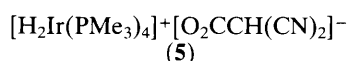
Stirring a solution of HIr(PMe₃)₄ (4) and malononitrile in tetrahydrofuran (THF) under a CO₂ pressure of 60 bar at 50 °C for 15 h afforded a suspension of a white solid. Cooling the mother liquor yielded pale yellow crystals of composition [H₂Ir(PMe₃)₄]⁺[O₂CCH(CN)₂]− (5). The i.r. spectrum of (5) (KBr mull) shows bands at 2197vs, 2173vs, 2142w, 1612vs, and 1330s cm⁻¹ which are assigned to the dicyanoacetate anion. Two bands at 2058vs and 2034vs cm⁻¹ are due to Ir–H vibrations. The room temperature ¹H n.m.r. spectrum of (5) shows two distorted triplets at δ −12.8 and −13.3 (J_{P-H} 21 Hz), assigned to the cis Ir–H₂ unit. The shape of the signal shows the complex to be fluxional.[5,6] The methyl protons of the PMe₃ ligands absorb as a doublet at δ 1.62 (J_{P-H} 7.8 Hz)

(cis-phosphines) and as a distorted triplet at δ 1.70 (trans-phosphines).[7] The structure of (5) is supported by the ¹³C n.m.r. spectrum [C=O, δ 171.7; C≡N, δ 132.2; (NC)₂C, δ 30.5] and the ³¹P n.m.r. spectrum (A₂B₂ pattern, δ −51.33 and −57.33 p.p.m., t, J 20.1 Hz). The crystal structure of complex (5) has been determined; see Figure 1.‡

The dicyanoacetate anions form a dimeric unit with an O(1)–O(2′) distance of 2.615 Å, which implies the existence of hydrogen atoms between the two O–O bridges. C(3) has sp² hybridization. Two hydrogen atoms and four PMe₃ groups
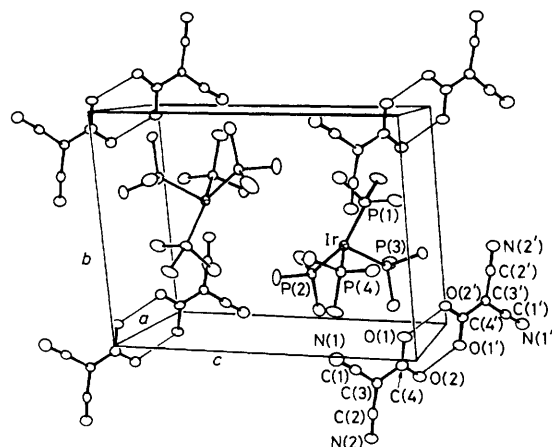

Figure 1. The molecular structure of [H₂Ir(PMe₃)₄]⁺[O₂CCH(CN)₂]− (5). The short distance O(1)–O(2′) of 2.615 Å implies the existence of a strong hydrogen bridge between these atoms. Selected bond lengths (Å) and angles (°): Ir–P(1) 2.318(2), Ir–P(2) 2.308(2), Ir–P(3) 2.350(2), Ir–P(4) 2.368(2), O(1)–C(4) 1.317(9), O(2)–C(4) 1.257(9); C(1)–C(3)–C(2) 117.7(7), C(1)–C(3)–C(4) 121.7(7), C(2)–C(3)–C(4) 120.5(7).

† The formulation of the anion as [O₂CCH(CN)₂]− is a simplification of the true structure; see description in the text.

surround the central iridium atom octahedrally, although during refinement the hydrogen atoms could not be located. The co-ordination of the phosphorus ligands around the iridium atom is distorted tetrahedral with Ir–P distance between 2.308 and 2.368 Å.

Analogous to $HIr(PMe_3)_4$ the complexes $[Ir(depe)_2]Cl$ (1) and $[Rh(dmpe)_2]Cl$ (6) react with malononitrile and CO_2 giving trans-$[HIr(depe)_2Cl]^+[O_2CCH(CN)_2]^-$ (7) and trans-$[HRh(dmpe)_2Cl]^+[O_2CCH(CN)_2]^-$ (8), respectively, characterized by i.r., and ^1H, ^{13}C, and ^{31}P n.m.r. spectroscopy. Complex (7) shows a ^1H n.m.r. quintet at δ −22.4 assigned to the Ir–H group. The ^{31}P n.m.r. spectrum shows only a single peak, showing the phosphorus atoms to be equivalent. The structure of (7) was confirmed by an X-ray diffraction study, details of which will be published elsewhere.

Comparison of complex (7) with the product of the reaction of $[Ir(depe)_2]Cl$ with acetonitrile and CO_2 postulated by Herskovitz[2] to be $[HIr(O_2CCH_2CN)(depe)_2]Cl$ show that they give the same ^1H n.m.r. shifts, indicating that both complexes have a similar structure.

The present results demonstrate that electron-rich transition metal centres enable the C–C linking to take place of activated alkanes and CO_2. This reaction offers an interesting way of making metal complexes and may serve as a basis for the creation of new catalytic reactions using carbon dioxide as a feedstock in chemical synthesis.

References

1 G. W. Parshall, *Acc. Chem. Res.*, 1975, **4**, 113; D. E. Webster, *Adv. Organomet. Chem.*, 1977, **15**, 147; J. C. Calabrese, M. C. Colton, T. Herskovitz, U. Klabunde, G. W. Parshall, D. L. Thorn, and T. H. Tulip, *Ann. N.Y. Acad. Sci.*, 1983, **415** (Catal. Trans. Met. Hydr.), 302.
2 A. D. English and T. Herskovitz, *J. Am. Chem. Soc.*, 1977, **99**, 1648.
3 G. W. Parshall, *Catalysis*, 1977, **1**, 335.
4 S. D. Ittel, C. A. Tolman, A. D. English, and J. P. Jesson, *J. Am. Chem. Soc.*, 1978, **100**, 7577.
5 P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Am. Chem. Soc.*, 1973, **95**, 75.
6 P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Am. Chem. Soc.*, 1971, **93**, 4701.
7 J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. (A)*, 1966, 77.