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FORMATION OF A HYDROXYMETHYLIRIDIUM(III) COMPOUND AND ADDITION OF THE O–H BOND TO BOUND ACETONITRILE *

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Summary

The hydridoformyliridium complex $[IrH(CHO)(PMe_3)_4][PF_6]$ (**2**) reacts with HBF_4/diethyl ether in acetonitrile to form the hydroxymethyl complex $[Ir(CH_2OH)(CH_3CN)(PMe_3)_4][PF_6][BF_4]$ (**4**). A hydrido hydroxycarbene complex **3** is believed to be an intermediate in this reaction. The acetonitrile ligand of compound **4** undergoes base-catalyzed attack by the oxygen atom of the hydroxymethyl group to form the metallacycle compound $[Ir(CH_2OC(CH_3)=NH)(PMe_3)_4][PF_6][BF_4]$ (**5**). Compound **5** cocrystallizes with $[HPMe_3][BF_4]$ in the monoclinic space group $P2_1/c$, a 13.772(2), b 13.436(2), c 19.506(3) Å, β 90.02(1)°, V 3609 Å^3, $Z = 4$. Precision of the X-ray structural results is limited by disorder of all the anionic groups. Refinement of 374 variables on 5312 reflections with $F_{obs}^2 > 2\sigma(F_{obs}^2)$ has converged at $R = 0.079$, $R_w = 0.091$.

Introduction

In the years following its discovery the transition metal-bound hydroxymethyl group ($M–CH_2OH$) has been the subject of considerable research, much of it focusing on carbonylation or CO hydrogenation chemistry [1–17]. To date most of the reported carbonylation attempts have been disappointing and the intermediacy of the hydroxymethyl group in catalytic CO hydrogenation remains arguable. Yet the hydroxymethyl group is still a fascinating entity in its own right, presenting the chemist with both a formidable synthetic challenge and a remarkable range of reactivity. This reactivity includes the versatile chemistry expected of alcoholic OH bonds (acylation or esterification [16,18], silylation [16,17], ether formation [4–7,15,19], deprotonation [13,16]) as well as surprisingly facile C–O [7,13], C–H [14,18], and M–C [13,17] bond cleavage reactions.

* Dedicated to Prof. S. Otsuka on the occasion of his 65th birthday.
** Contribution No. 3486.

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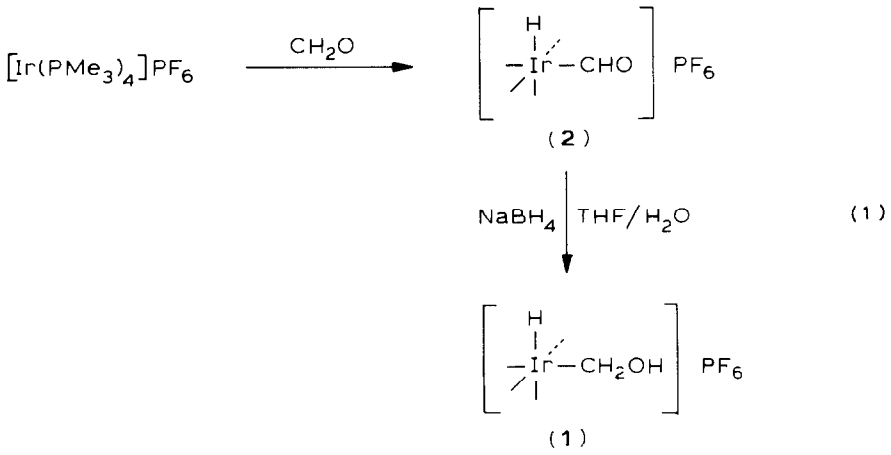
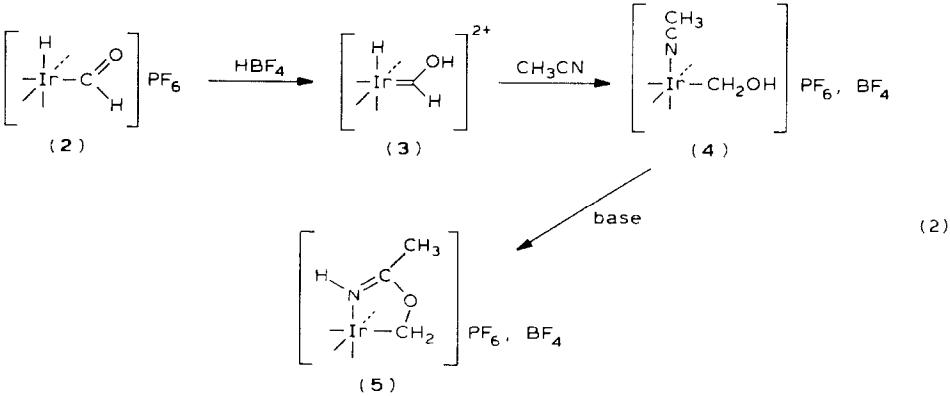


Our studies of hydroxymethyl compounds of iridium have arisen from studies of the reactions of iridium compounds with formaldehyde. The first reported iridium hydroxymethyl complex, compound **1**, was initially prepared by chemical reduction of the formaldehyde-derived hydrido formyl compound **2** (eq. 1) [12,13]. More recently we have prepared another hydroxymethyliridium compound from compound **2** by the reactions outlined in eq. 2. In this reaction sequence the hydroxymethyl group is assembled by O-protonation of the formyl group, first forming the hydrido hydroxycarbene complex **3**, followed by hydrogen atom migration from the metal center to the carbon atom. Solvation by acetonitrile completes the synthesis of the previously-unreported hydroxymethyl complex, compound **4**. While compound **4** can be detected in solution and isolated as an impure solid, it is unstable and undergoes an intramolecular cyclization reaction to form compound **5**. In this article we describe in detail the sequence of reactions leading to compounds **4** and **5** and the crystal and molecular structure of the metallacyclic compound **5**.

Results

The protonation reaction. The hydridoformyl complex **2** reacts immediately with a stoichiometric amount of HBF_4/diethyl ether in acetonitrile solution to form the hydroxymethyl compound **4** in variable yield (30 to 70% by ^1H NMR analysis). The



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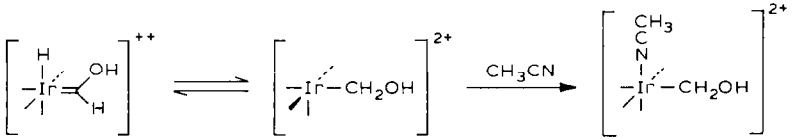
remaining products have not yet been characterized. We believe the reaction proceeds by the sequence of eq. 2, where a hydroxycarbene complex **3** is an intermediate. In fact, if HBF_4/diethyl ether is added to a methylene chloride solution of compound **2**, a white precipitate forms immediately. IR analysis of this material reveals O–H and Ir–H stretching bands at 3400 cm^{-1} (w, vbr) and 2060 cm^{-1} respectively, with no C=O stretching band, and we tentatively assign the (hydrido)(hydroxycarbene) structure **3** to this compound. Adequate characterization of this material has been impossible because it decomposes in the solid state within 24 h at room temperature, and it reacts immediately with pyridine and acetonitrile and is insoluble in other solvents. In pyridine-d_5 solution, the only ^1H NMR signals observable are those of the starting formyl compound **2** and H-pyridine$^+$, suggesting the protonation reaction is reversible. When compound **3** is exposed to acetonitrile, compound **4** is the only characterizable species present in solution (^1H NMR); see below.

The hydridoformyl compound **2** does not react with the milder acid, anhydrous HCl, and the starting material is recovered. Commercial HPF_6/ether and trifluoromethanesulfonic acid both do protonate compound **2** but the reactions are less clean than that of HBF_4/diethyl ether and are still under investigation.

The hydroxymethyl complex. If complex **3** is dissolved in acetonitrile or if protonation of compound **2** is carried out in acetonitrile solution, the solvated hydroxymethyl compound **4** is formed. Most likely, in solution an equilibrium is established between the (hydrido)(hydroxycarbene) complex **3** and the product of hydrogen atom migration from the metal center to the α-carbon atom (eq. 3), and this equilibrium is trapped by rapid and strong solvent coordination at the vacant site to form compound **4** irreversibly.



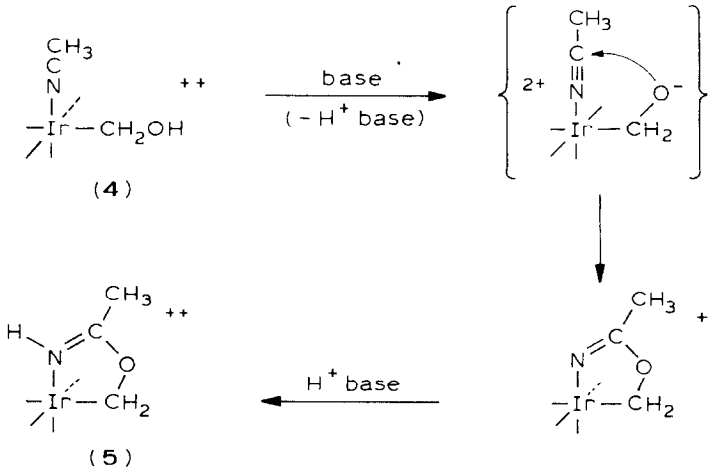
(3) (4) (3)

Compound **4** has not been isolated in pure form, as its tendency to undergo further reaction (see below) makes its separation from reaction byproducts difficult. However, impure samples (ca. 85% **4**, 5% compound **5**, 10% byproducts) are adequate for its characterization. Spectroscopic studies of a sample of compound **4** isolated from CH_3CN solution unambiguously establish the presence of bound CH_3CN (IR: 2325, 2300 cm^{-1}; ^1H NMR (CD_3CN solution): 1 CH_3CN:/4 PMe_3 groups by integration), an OH group (IR: 3525, 3575 (br) cm^{-1}), the Ir–CH_2O entity (^1H NMR), and the four PMe_3 groups (^1H NMR) (see Experimental section).

The intramolecular cyclization reaction. Compound **4** is unstable in acetonitrile solution and undergoes further reaction to form the metallacyclic compound **5** (eq. 2). The rate of this reaction varies considerably from sample to sample. When small amounts of base (e.g. pyridine, PMe_3) are added this cyclization reaction proceeds rapidly and is apparently complete within time-of-mixing at room temperature. In the absence of base, compound **4** persists long enough to be characterized by ^1H NMR analysis, and in some cases for several hours. A slight excess of HBF_4/diethyl ether appears to suppress the cyclization reaction but also causes some decomposi-

tion of compound **4**, with signals for $HPMe_3^+$ appearing in the ^1H NMR spectrum.

These results are consistent with a base-catalyzed reaction (eq. 4), where the bound acetonitrile group undergoes nucleophilic attack by the oxygen atom of the deprotonated hydroxymethyl group. In the absence of added base, adventitious impurities, BF_4 or PF_6 counterions, walls of the reaction flask, and/or solvent molecules function as the proton carrier and allow this reaction to proceed (albeit slowly), thus limiting the solution lifetime of compound **4**.



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The crystal and molecular structure of compound (5). Repeated attempts to obtain crystals of compounds **4** or **5** suitable for X-ray diffraction studies were unsuccessful. However, in one experiment an acetonitrile-d_3 solution of the hydridoformyl

TABLE 1

CRYSTALLOGRAPHIC DATA OF COMPOUND 5

Complex	$[\overline{Ir(CH_2OC(CH_3)=NH)}(PMe_3)_4][HPMe_3][PF_6][BF_4]_2$
Formula	$C_{18}H_{52}N_1O_1B_2F_{14}Ir_1P_6$
Formula Weight	964.3
Space group	$P2_1/c$
a, Å	13.772(2)
b, Å	13.436(2)
c, Å	19 506(3)
β, deg.	90.02(1)
V, Å^3	3609
Z	4
Temp., °C	−100
Radiation	Mo-K_α 0.71069 Å from monochromator
2θ limits, deg.	4.0–55.0
Total no. of unique observations	7911
Data, $F_0 > 2\sigma(F_0)$	5312
Final no. of variables	374
R, R_w	0.079, 0.091

TABLE 2

INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Ir(1)–P(1)	2.304(4)	P(3)–C(31)	1.785(18)
Ir(1)–P(2)	2.384(4)	P(3)–C(32)	1.802(22)
Ir(1)–P(3)	2.390(5)	P(3)–C(33)	1.836(24)
Ir(1)–P(4)	2.398(4)	P(4)–C(41)	1.813(21)
Ir(1)–N(1)	2.080(12)	P(4)–C(42)	1.719(24)
Ir(1)–C(2)	2.142(17)	P(4)–C(43)	1.820(33)
P(6)–F(61)	1.551(25)	P(5)–C(51)	1.811(26)
P(6)–F(62)	1.755(71)	P(5)–C(52)	1.626(33)
P(6)–F(62A)	1.706(46)	P(5)–C(53)	1.751(25)
P(6)–F(63)	1.555(51)	F(11)–B(1)	1.391(20)
P(6)–F(63A)	1.671(53)	F(12)–B(1)	1.425(21)
P(6)–F(64)	1.491(35)	F(13)–B(1)	1.489(26)
P(6)–F(65)	1.755(57)	F(14)–B(1)	1.219(23)
P(6)–F(65A)	1.486(62)	F(21)–B(2)	1.372(23)
P(6)–F(66)	1.642(62)	F(22)–B(2)	1.127(30)
P(6)–F(66A)	1.586(40)	F(23)–B(2)	1.429(22)
P(1)–C(11)	1.798(18)	F(24)–B(2)	1.383(29)
P(1)–C(12)	1.789(18)	O(3)–C(2)	1.444(19)
P(1)–C(13)	1.812(19)	O(3)–C(4)	1.330(20)
P(2)–C(21)	1.788(25)	N(1)–C(4)	1.272(20)
P(2)–C(22)	1.815(18)	C(4)–C(5)	1.477(25)
P(2)–C(23)	1.873(20)	N(1)–H(1)	0.91
P(1)–Ir(1)–P(2)	93.7(2)	Ir(1)–P(4)–C(41)	114.5(7)
P(1)–Ir(1)–P(3)	97.9(2)	Ir(1)–P(4)–C(42)	125.1(9)
P(1)–Ir(1)–P(4)	98.3(2)	Ir(1)–P(4)–C(43)	114(1)
P(2)–Ir(1)–P(3)	92.2(2)	C(11)–P(1)–C(12)	101(1)
P(2)–Ir(1)–P(4)	166.5(2)	C(11)–P(1)–C(13)	99(1)
P(3)–Ir(1)–P(4)	92.2(2)	C(12)–P(1)–C(13)	101(1)
P(1)–Ir(1)–N(1)	165.3(3)	C(21)–P(2)–C(22)	99(1)
P(2)–Ir(1)–N(1)	83.4(4)	C(21)–P(2)–C(23)	105(1)
P(3)–Ir(1)–N(1)	96.6(4)	C(22)–P(2)–C(23)	102(1)
P(4)–Ir(1)–N(1)	83.4(4)	C(31)–P(3)–C(32)	100(1)
P(1)–Ir(1)–C(2)	89.1(4)	C(31)–P(3)–C(33)	102(1)
P(2)–Ir(1)–C(2)	85.5(5)	C(32)–P(3)–C(33)	99(1)
P(3)–Ir(1)–C(2)	172.8(4)	C(41)–P(4)–C(42)	104(1)
P(4)–Ir(1)–C(2)	88.5(5)	C(41)–P(4)–C(43)	98(1)
N(1)–Ir(1)–C(2)	76.3(5)	C(42)–P(4)–C(43)	97(2)
Ir(1)–P(1)–C(11)	120.6(6)	C(51)–P(5)–C(52)	114(2)
Ir(1)–P(1)–C(12)	118.7(6)	C(51)–P(5)–C(53)	112(2)
Ir(1)–P(1)–C(13)	113.6(7)	C(52)–P(5)–C(53)	116(2)
Ir(1)–P(2)–C(21)	116.7(8)	C(2)–O(3)–C(4)	119(1)
Ir(1)–P(2)–C(22)	112.9(6)	Ir(1)–N(1)–C(4)	119(1)
Ir(1)–P(2)–C(23)	119.1(7)	Ir(1)–C(2)–O(3)	109(1)
Ir(1)–P(3)–C(31)	114.8(6)	O(3)–C(4)–N(1)	117(1)
Ir(1)–P(3)–C(32)	120.7(8)	O(3)–C(4)–C(5)	116(2)
Ir(1)–P(3)–C(33)	116.9(9)	N(1)–C(4)–C(5)	126(2)

compound **2** was treated with PMe_3 and HBF_4/diethyl ether in the hope that the hydroxymethyl compound $[Ir(CH_2OH)(PMe_3)_5]^{2+}$ might be detected by ^1H NMR analysis. This compound was not formed, and $HPMe_3^+$ and the metallacycle compound **5** were the only characterizable compounds present in the solution (^1H

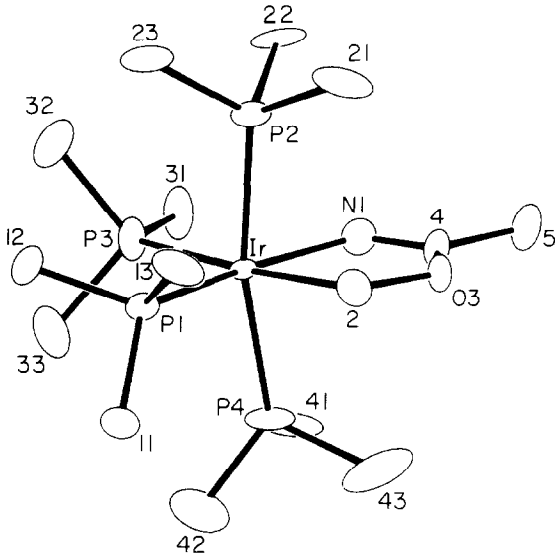
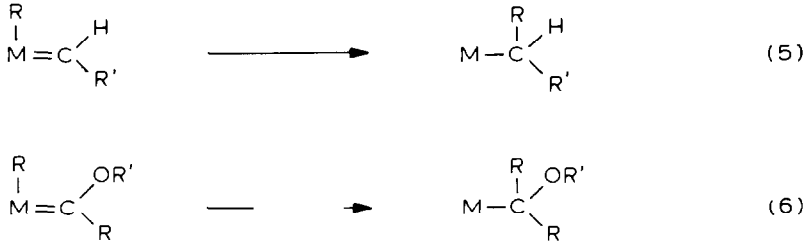


Fig. 1. A perspective drawing of the dicationic complex **5**. Thermal ellipsoids are drawn at the 50% probability level. Carbon atoms are labeled with their numbers only and all hydrogen atoms are omitted.

NMR analysis). From this solution, single crystals were grown by dichloromethane vapor diffusion. The crystallographic and refinement data are summarized in Table 1. Unfortunately the crystal lattice contains, in addition to the desired $[Ir(CH_2OC(CD_3)=NH)(PMe_3)_4]$ dication with PF_6 and BF_4 anions, the $HPMe_3$ cation with a corresponding BF_4 anion. Furthermore, the $HPMe_3$ cation, the PF_6 anion, and the BF_4 anions are disordered at their respective lattice sites. These disordered species were modelled as well as possible in the usual manner (see Experimental section) but the agreement indices remain relatively high for a low-temperature, heavy-atom structure (see Table 1). Fortunately the organometallic dication is well-ordered (see Fig. 1) and selected interatomic distances and angles are listed in Table 2. Despite their limited precision the bond distances are fully consistent with the valence bond representations of compound **5** that have been drawn in eq. 2 and 4. In particular, Ir–C, C–O, and Ir–N distances within the metallacyclic ring are normal for single bonds, and the C=N distance is that expected for a double bond.

Discussion

Hydrogen atom migration. Throughout our discussion we will refer to the formation of the C–H bond as "hydrogen atom migration" although it cannot be distinguished from "carbene insertion" in the reactions we describe. Several examples are already known of these migration reactions (eq. 5), where a terminal alkylidene group serves as the migration terminus for an adjacent hydrido hydrogen atom or alkyl group [13,18,20–23]. Examples are also known of hydrido hydrogen atom or alkyl group migration to an -oxycarbene group, eq. 6 [10,24–26]. Closely related to the present study is the earlier report by Roper and coworkers of hydrido



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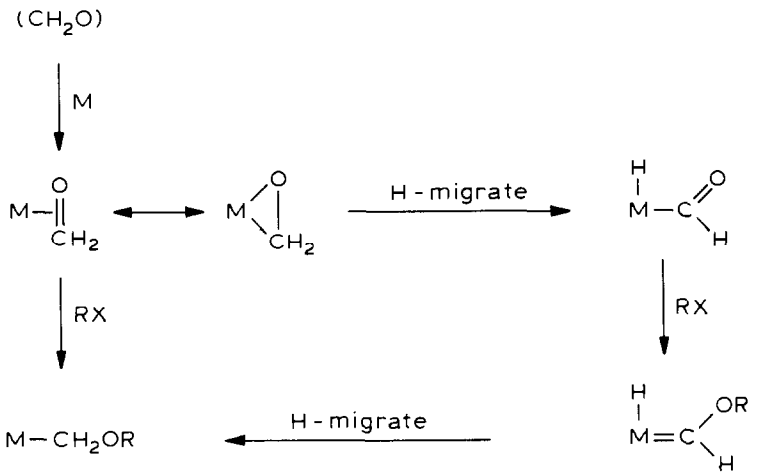
(6)

hydrogen atom migration to an osmium methoxycarbene group (eq. 6, R = H, R′ = CH_3, M = Os) [10]. The conversion of compound **3** to compound **4** has a delightful aspect in common with the reported osmium chemistry: hydrido hydrogen atom migration from the metal to the carbon atom restores the very same C–H bond that was cleaved in the initial formation of the hydridoformyl complex (Scheme 1). Thus in principle, the final product (the hydroxy- or alkoxy-methyl complex) could have been obtained by protonating or alkylating an intact CH_2O entity [8,10,11,27]; C–H activation or migration reactions are not fundamentally necessary. However, CH_2O (formaldehyde) does not remain intact in the presence of most PMe_3–Ir complexes [12] and the final -oxymethyl compounds **4** and **5** are available only by the H-migration reaction sequence.

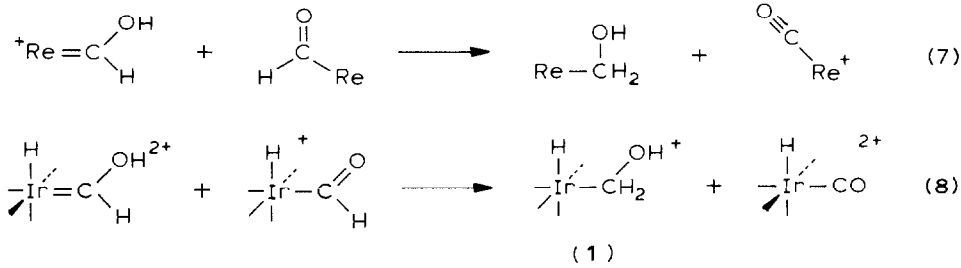


SCHEME 1

Yet another similarity between the osmium system mentioned above and the present iridium system is that hydrogen atom migration from metal to carbon leaves a vacant coordination site. This in turn scavenges an available donor ligand, water in the osmium example and acetonitrile in the iridium system (eq. 3). We will describe elsewhere our experiments with another set of compounds, where the nature of available donor ligand(s) has a remarkable effect on hydrogen migration reactions [18].

Implicit in our discussion of this chemistry is the assumption that hydrogen atom migration is strictly intramolecular. It must be noted that the first example of hydrogen atom migration to a protonated formyl group was an intermolecular reaction (eq. 7) [28]. Such an intermolecular reaction in the present system may be

responsible for the as-yet-uncharacterized byproducts formed in the protonation of compound **2**. Compounds **4** and **5**, however, are almost certainly formed by intramolecular reactions: the hydroxymethyl compound that would be formed in an intermolecular reaction (eq. 8) is the known compound **1**, which is not present in any of these reaction mixtures.



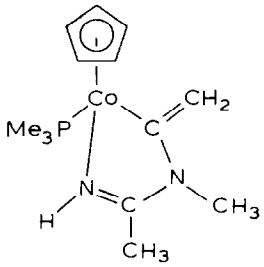
(7)

(8)

(1)

OH addition to acetonitrile and the metallacyclic structure. The many contributions made by Professor Otsuka and his coworkers include studies of hydroxometal compounds and their uses in hydration of nitriles and CO [29,30]. In either case, coordination to the metal center serves to activate the triple bond of the organic molecule toward nucleophilic attack by hydroxide. The conversion of compound **4** to compound **5** provides another example of this reaction; the acetonitrile molecule, bonded to the dicationic $[Ir(CH_2OH)(PMe_3)_4]$ fragment, is rendered extremely susceptible to attack by the adjacent oxygen nucleophile. As outlined in eq. 4 we believe the deprotonated hydroxymethyl group ($Ir-CH_2-O$, which is essentially an alkoxide held proximate to the acetonitrile ligand) is the reactive form of the oxygen nucleophile. We have previously observed that the deprotonated hydroxymethyl group, alternatively viewed as an η^1 formaldehyde ligand, is a reactive species [13].

Other compounds are known where a metallacycle unit has been constructed by nucleophilic addition to an organic nitrile molecule. One such compound, closely related to the metallacycle **5**, is the cobalt metallacycle **6**, formed by nucleophilic attack of a nitrogen atom on coordinated acetonitrile [31].



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Experimental

All reactions were carried out at room temperature using standard inert atmosphere techniques and dried, degassed solvents. Compound **2** was prepared according

to previously-published methods [12]. HBF_4/diethyl ether was used as supplied by Aldrich Chemical Co. NMR studies were carried out using Nicolet NIC-200, NIC-360 and Varian FT80A (^1H) and Bruker WM-400 (^{13}C) spectrometers with ambient probe temperatures (25–30 °C). All chemical shifts are reported in ppm downfield from external Me_4Si.

Preparation of [Ir(CH$_2$OH)(CH$_3$CN)(PMe$_3$)$_4$][PF$_6$][BF$_4$] (4)

A solution of 0.12 g [IrH(CHO)$(PMe_3)_4$][PF_6] (compound **2**) in 1 ml CH_3CN was treated with a solution of HBF_4/diethyl ether (0.025 g) in 0.5 ml CH_3CN. After stirring the solution 2 min diethyl ether was added; the resulting white precipitate was collected and washed with CH_2Cl_2, yield 0.095 g (66%). IR (Nujol, cm^{-1}): 3525, 3575 br; 2325, 2300 m; 2085 (impurity). ^1H NMR (CD_3CN): $P(CH_3)_3$, 1.59, d (11 Hz), 1.61, d (8 Hz), 1.63, t (4 Hz); CH_3CN, 1.93, s; Ir–CH_2, 4.2, t (7 Hz) of d (3 Hz).

Preparation of [Ir(CH$_2$OC(CH$_3$)=NH)(PMe$_3$)$_4$][PF$_6$][BF$_4$] (5)

Method a. Pyridine-d_5 (0.25 ml) was added to the above CD_3CN solution of compound **4**. The ^1H NMR spectrum of the resulting solution, run immediately after preparation, revealed the complete conversion of compound **4** to compound **5**. ^1H NMR: $P(CH_3)_3$, 1.53, t (4 Hz), 1.60, d (10 Hz), 1.71, d (8 Hz); C–CH_3, 1.91, s; Ir–CH_2, 5.58, t (13 Hz) of pseudo-t (1.5 Hz).

Method b. A solution of 0.67 g compound **2** in 5 ml CH_3CN was treated with 0.17 g HBF_4/diethyl ether and stirred 5 min. Pyridine (0.1 g) was added and the solution was evaporated to dryness. The residue was washed with CH_2Cl_2 and redissolved in CH_3CN. Addition of diethyl ether caused 0.25 g white solid to precipitate. This was redissolved in CH_3CN and recrystallized by vapor diffusion of CH_2Cl_2, yield 0.14 g (17%). IR (Nujol, cm^{-1}): 3330 s, 1620 s. ^1H NMR (pyridine-d_5): $P(CH_3)_3$, 1.76, t (4 Hz), 1.84, d (10 Hz), 1.93, d (8 Hz); C–CH_3, 2.51, s; Ir–CH_2, 5.78, t (13 Hz) of pseudo-t (1 Hz); N–H, 13.7, br s (disappears with D_2O addition). ^{13}C NMR (pyridine-d_5): $P(CH_3)_3$, 15.4, t (18 Hz), 19.2, d (41 Hz), 19.4, d (31 Hz); C–CH_3, 16.7, s; Ir–CH_2, 67.2 d (72 Hz) of m. Anal Found: C, 22.62, 22.63; H, 5.05, 4.97%. $C_{15}H_{42}N_1O_1B_1F_{10}Ir_1P_5$ calcd.: C, 22.51; H, 5.29%.

X-Ray data collection and structure solution and refinement

Dichloromethane vapor was allowed to diffuse slowly into a solution of compound **5** and [$HPMe_3$][BF_4] in CD_3CN, resulting in a crystalline deposit after several days. An irregularly-shaped fragment from this deposit was used for the X-ray data collection, using methods standard in our laboratory [32]. Crystallographic data are included in Table 1.

The structure was solved using Patterson and Fourier methods. The disorder of the $HPMe_3$ cation and BF_4 and PF_6 anions became apparent at an early stage in the refinement. The disordered PF_6 anion was modelled by including the extra atoms F(62A), F(63A), F(65A), F(66A) with occupancy of 0.5 and correspondingly diminished occupancies of the other component. However, the disorder in the $HPMe_3$ cation and BF_4 anions could not be resolved and is partially accommodated by the "thermal" anisotropy of the atoms of these groups. All positional and thermal parameters and interatomic distances and angles involving these groups are

TABLE 3

FRACTIONAL COORDINATES (×10000) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS

Atom	x	y	z	B_{iso}^{a}
Ir(1)	2064.4(4)	7845 8(4)	5005.0(3)	2 2(1)′
P(1)	3007(3)	8461(3)	5884(2)	3 1(1)′
P(2)	801(3)	7306(4)	5752(2)	3.5(1)′
P(3)	2755(4)	6216(4)	4950(2)	3 8(1)′
P(4)	3030(4)	8419(5)	4062(2)	4 7(2)′
P(5)	3154(5)	2387(6)	2504(4)	7 0(2)′
P(6)	2942(10)	12277(12)	5058(8)	13.4(5)′
F(11)	−220(9)	9226(9)	8559(6)	5.9(4)′
F(12)	918(10)	8629(9)	7871(7)	6.8(4)′
F(13)	750(11)	10303(9)	7998(8)	7.5(5)′
F(14)	−378(11)	9359(13)	7426(7)	9.0(6)′
F(21)	4121(14)	5323(17)	7222(9)	12.2(8)′
F(22)	5558(19)	5285(35)	7568(14)	26 4(22)′
F(23)	5352(15)	5640(13)	6539(8)	10.4(7)′
F(24)	4889(25)	4188(18)	6783(16)	20.0(14)′
F(61)	3713(17)	11526(19)	4795(12)	13.3(6)
F(62)	3482(53)	11997(53)	5850(37)	19.5(22)
F(62A)	2679(34)	11628(36)	5786(24)	11.6(11)
F(63)	2302(34)	11350(39)	5214(29)	12.9(13)
F(63A)	2342(35)	11524(45)	4524(31)	13 4(14)
F(64)	2039(26)	12781(27)	5297(19)	19 7(11)
F(65)	2395(37)	12315(52)	4246(29)	14.0(15)
F(65A)	2544(46)	13050(50)	4592(36)	16 5(19)
F(66)	3592(45)	13159(46)	4698(32)	16.8(18)
F(66A)	3622(28)	13001(30)	5486(21)	10.2(9)
O(3)	585(9)	9199(9)	4435(6)	4.4(4)′
N(1)	1019(10)	7630(9)	4250(6)	2 8(3)′
C(2)	1300(13)	9233(12)	4977(9)	3 5(4)′
C(4)	469(14)	8354(13)	4091(9)	3 8(5)′
C(5)	−324(16)	8335(17)	3580(12)	5.7(7)′
C(11)	4022(14)	9262(17)	5706(9)	4.9(6)′
C(12)	3542(16)	7603(14)	6475(9)	4.7(6)′
C(13)	2348(15)	9261(17)	6469(10)	5.3(6)′
C(21)	−174(15)	8160(19)	5896(12)	6.7(8)′
C(22)	113(16)	6268(16)	5408(9)	5.8(7)′
C(23)	1124(16)	6832(16)	6626(9)	5.3(6)′
C(31)	2294(17)	5450(15)	4276(10)	5.5(6)′
C(32)	2643(21)	5367(16)	5661(10)	6.6(8)′
C(33)	4070(16)	6136(20)	4808(14)	7.2(9)′
C(41)	2987(16)	7628(21)	3309(9)	6 9(8)′
C(42)	4229(19)	8766(34)	4114(12)	11.8(15)′
C(43)	2591(33)	9559(24)	3664(16)	13 5(16)′
C(51)	2389(22)	3462(20)	2654(21)	10.8(13)′
C(52)	3839(28)	2086(28)	3151(17)	11.2(14)′
C(53)	2515(22)	1412(23)	2114(21)	11.3(14)′
B(1)	179(17)	9370(16)	7912(9)	3.8(6)′
B(2)	5076(12)	5070(13)	7125(8)	2 1(4)′
H(1)	633	7095	4155	0.7
H(2′)	979	9337	5413	2.1
H(2″)	1746	9765	4901	6.6

[a] Unprimed values given for isotropically-refined atoms

highly suspect. Final refinement data are included in Table 1, and final positional and equivalent thermal parameters for all nonhydrogen atoms are listed in Table 3. Positional and thermal parameters for the hydrogen atoms on C(2) and N(1) were refined and are included in Table 3. Anisotropic thermal parameters (Table 4), positions of the remaining hydrogen atoms (Table 5), and final values for F_{obs} and F_{calc} (Table 6) are available as Supplementary Material *.

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