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Solid-State Reactions of Iridium(I)–1,5-Cyclooctadiene Compounds with CO: Synthesis of Cationic (1,5-Cyclooctadiene)carbonyliridium(I) Complexes

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Summary: *$[Ir(COD)(CO)_2(L)]ClO_4$ (**1**) and $[Ir(COD)(CO)(L)_2]ClO_4$ (**2**) (COD = 1,5-cyclooctadiene; L = PPh_3 (**a**), $AsPh_3$ (**b**)) have been prepared from the solid-state reactions of $[Ir(COD)(L)(PhCN)]ClO_4$ (**3**) and $[Ir(COD)(L)_2]ClO_4$ (**4**), respectively, with CO (1 atm) at 25 °C. The products **1** and **2** have been characterized by conventional analytical and spectroscopic methods as well as single-crystal X-ray crystallographic analysis for $[Ir(COD)(CO)_2(PPh_3)]ClO_4$ (**1a**) and $[Ir(COD)(CO)_2(AsPh_3)]ClO_4$ (**1b**).*

Transition-metal complexes containing olefins and CO have been studied because they could be intermediates of metal-catalyzed carbonylation and the related reactions of organic compounds.[1] Iridium(I) complexes of 1,5-cyclooctadiene (COD) have been investigated probably because they react with other ligands to give various derivatives which are useful catalysts for organic reactions.[2] Numerous iridium(I) complexes containing CO have been reported;[3] however, there are only a few examples of Ir–(COD) complexes containing CO.[4] The Ir–(COD)(CO) complexes were prepared by the reactions of Ir–CO complexes with COD, since the coordinated COD is usually replaced by CO in the reactions of Ir–(COD) complexes in solution.[4c,5] To our knowledge, no report has been made on a monomeric iridium(I)–(η^4–COD)(CO) complex.

Recently, it has been reported that various reactions of Rh and Co complexes can occur between solid metal complexes and gaseous molecules such as nitrogen and hydrogen at high temperature (up to 65 °C), and Co complexes rearrange between Co–(hydrido)(alkynyl) and Co–(vinylidene) in both solid state and solution.[6] An iridium(I)–COD complex, $[Ir(COD)(PPh_3)_2]_3PW_{12}O_{40}$, reacts with D_2 in the solid state to give highly deuterated cyclooctene and cyclooctane through a multiple and sequential C–H activation process.[7] It has been also investigated both in solution and in the solid state that iridium complexes lose hydrogen reversibly[8] and undergo interconversion between classical dihydride and nonclassical dihydrogen.[9] Dichlorotetracarbonyldirhodium, $[Rh(CO)_2Cl]_2$, has been obtained by the reaction of $RhCl_3 \cdot xH_2O$ with CO in the solid state at 100 °C.[10] On the other hand, the complexes $M(OClO_3)(CO)(PPh_3)_2$ and $M(OH)(CO)(PPh_3)_2$ (M = Ir, Rh) react with gaseous SO_2 and CO_2 to give $M(SO_2)(OClO_3)(CO)(PPh_3)_2$ and $M(CO_2)(OH)(CO)(PPh_3)_2$, respectively, in the absence of a solvent.[11] A ruthenium complex, $Ru(OEP)(py)_2$ (OEP = octaethylporphyrin, py = pyridine), forms the metal–metal-bonded porphyrin dimer in the solid state at high temperature.[12] In this note we wish to report some new cationic iridium(I)–(COD)(CO) complexes, $[Ir(COD)(CO)_2(L)]ClO_4$ (**1**) and $[Ir(COD)(CO)(L)_2]ClO_4$ (**2**) (L = PPh_3 (**a**), $AsPh_3$ (**b**)), prepared from the reactions of the Ir^I–(COD) complexes $[Ir(COD)(L)(PhCN)]ClO_4$ (**3**) and $[Ir(COD)(L)_2]ClO_4$ (**4**) with CO in the absence of a solvent at room temperature.

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Experimental Section

Precautions must be taken, since perchlorate salts are hazardously explosive.

Instruments. NMR spectra were recorded on a Varian Gemini 300 or Bruker AC-200 pulsed FT spectrometer at 300 or 200 MHz. Other instruments used in this work were a Shimadzu IR-440 spectrophotometer and a CARLO ERBA EA1108 elemental analyzer.

Synthesis. The Ir^I–(COD) complexes [Ir(COD)(L)(PhCN)]-ClO_4 (**3**) and [Ir(COD)(L)$_2$]ClO_4 (**4**) (L = PPh_3 (**a**), $AsPh_3$ (**b**)) were prepared by the literature methods.[13-15]

[Ir(COD)(CO)$_2$(PPh$_3$)]ClO$_4$·CH$_2$Cl$_2$ (1a·CH$_2$Cl$_2$). Orange-red microcrystals of [Ir(COD)(L)(PhCN)]ClO_4 (**3a**; 0.3 g, 0.39 mmol) in a 50-mL round-bottom flask reacted with CO (P_{CO} = 1 atm) at room temperature in the absence of a solvent for 24 h; during that time the solid slowly turned beige. Recrystallization of the beige solid with CH_2Cl_2/*n*-hexane gave red crystals of [Ir(COD)(CO)$_2$(PPh$_3$)]ClO_4·CH_2Cl_2 (**1a**·CH_2Cl_2): yield 0.27 g, 86%; mp 152.4 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.65–7.42 (m, 15 H, Ph), 5.305 (s, 2 H, CH_2Cl$_2$), 4.44 (s, 4 H, COD olefinic), 2.83–2.60 (m, 8 H, COD methylene) ppm; ^{13}C NMR (75.43 MHz, $CDCl_3$, 25 °C) δ 171.02 (d, J_{P-C} = 10.64 Hz, $C{\equiv}O$), 133.85–127.20 (m, Ph), 83.69 (s, COD olefinic), 53.52 (s, CH_2Cl_2), 33.46 (s, COD methylene) ppm; IR (Nujol, cm^{-1}) 2065 s, 2016 s ($C{\equiv}O$), 1100 br, s (ClO_4). Anal. Calcd for $C_{29}H_{29}Cl_3IrO_6P$: C, 43.37; H, 3.64. Found: C, 43.49; H, 3.60.

[Ir(COD)(CO)$_2$(AsPh$_3$)]ClO$_4$·CH$_2$Cl$_2$ (1b·CH$_2$Cl$_2$). Compound **1b** was synthesized from the reaction of [Ir(COD)(AsPh$_3$)(PhCN)]ClO_4 (**3b**; 0.3 g, 0.37 mmol) with CO in the same manner as described for **1a**, and recrystallization of brown solid gave pale red crystals of [Ir(COD)(CO)$_2$(AsPh$_3$)]ClO_4·CH_2Cl_2 (**1b**·CH_2Cl_2): yield 0.24 g, 77%; mp 148.3 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C) δ 7.61–7.27 (m, 15 H, Ph), 5.30 (s, 2 H, CH_2Cl$_2$), 4.62 (s, 4 H, COD olefinic), 2.72–2.52 (m, 8 H, COD methylene) ppm; ^{13}C NMR (50.30 MHz, $CDCl_3$, 25 °C) δ 168.86 (s, $C{\equiv}O$), 132.28, 130.15, 129.11 (Ph), 81.34 (s, COD olefinic), 53.49 (s, CH_2Cl_2), 33.68 (s, COD methylene) ppm; IR (Nujol, cm^{-1}) 2068 s, 2020 s ($C{\equiv}O$), 1100 br, s (ClO_4). Anal. Calcd for $C_{29}H_{29}Cl_3IrO_6As$: C, 41.12; H, 3.45. Found: C, 41.18; H, 3.31.

Crystals of **1a** and **1b** for X-ray crystal structure determination were obtained by slow evaporation of the solutions of **1a** and **1b** in CH_2Cl_2/*n*-hexane (3:1) at room temperature under nitrogen.

[Ir(COD)(CO)(PPh$_3$)$_2$]ClO$_4$ (2a) and [Ir(COD)(CO)(AsPh$_3$)$_2$]ClO$_4$ (2b). Deep red microcrystals of [Ir(COD)(PPh$_3$)$_2$]ClO_4 (**4a**; 0.3 g, 0.32 mmol) in a 10-mL round-bottom flask reacted with CO (P_{CO} = 1 atm) at room temperature in the absence of a solvent to give the beige solid **2a** within 30 min. The compound **2a** further reacts with CO to give **5** very slowly (see text). Data for **2a**: mp 123 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$, –60 °C) δ 7.57–7.01 (m, 30 H, Ph), 5.30 (br s, 4 H, COD olefinic), 2.34–2.106 (m, 8 H, COD methylene) ppm; IR (Nujol, cm^{-1}) 2005 s ($C{\equiv}O$), 1100 br, s (ClO_4). Anal. Calcd for $C_{45}H_{42}ClIrO_5P_2$: C, 56.75; H, 4.44. Found: C, 56.59; H, 4.42.

Compound **2b** was produced in the same manner as described for **2a**: mp 110 °C dec; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C) δ 7.52–7.04 (m, 30 H, Ph), 4.32 (s, 4 H, COD olefinic), 2.24 (s, 8 H, COD methylene) ppm; ^{13}C NMR (50.30 MHz, $CDCl_3$, 25 °C) δ 172.84 (s, $C{\equiv}O$), 132.23–128.49 (Ph), 77.76 (s, COD olefinic), 32.82 (s, COD methylene) ppm; IR (Nujol, cm^{-1}) 1998 s ($C{\equiv}O$), 1100 br, s (ClO_4). Anal. Calcd for $C_{45}H_{42}ClIrO_5As_2$: C, 51.95; H, 4.07. Found: C, 52.14; H, 4.08.

Collection and Refinement of X-ray Data for 1a. A red crystal of dimensions 0.50 × 0.30 × 0.30 mm was mounted on a glass fiber in a random orientation. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated molybdenum radiation ($\lambda(K\alpha)$ = 0.710 73 Å) at ambient temperature (20 ± 1 °C). A preliminary diffractometric investigation indicated that **1a** belongs to the space group $Pna2_1$. The lattice constants were determined by the least-squares refinement of the diffraction geometry for 24 intense reflections having $7 < \theta < 12°$. Crystal parameters for the compound and information on the procedure used for data collection and refinement are given in Table I. Intensity data were collected by the ω–2θ scan technique. Data were collected by the 2θ value of 50°, and the ratio of peak counting time to background counting time was 2:1. A total of 2402 reflections were collected, of which 2230 were unique and not systematically absent. Lorentz and polarization corrections were applied to the data. An empirical absorption correction based on ψ scans was applied to the data. Relative transmission coefficients ranged from 0.552 to 1.000 with an average value of 0.799. The structure was solved by direct methods. Using 260 reflections (minimum *E* value of 1.20) and 9647 relationships, a total of 32 phase sets were produced. Only one atom was located from an *E*-map prepared from the phase set. The remaing non-hydrogen atoms were located in succeeding difference Fourier syntheses. The phenyl carbon atoms were refined with isotropic thermal parameters, while all the other non-hydrogen atoms were anisotropically refined. Hydrogen atoms were located and added to the structure factor calculations, but their positions were not refined. The structure was refined by full-matrix least squares, where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight *w* is defined as $4F_o^2/\sigma(F_o^2)$. All calculations were performed on a VAX computer using the MolEN (Enraf-Nonius) program.[16] The final positional parameters and isotropic equivalents of anisotropic thermal parameters for **1a** are listed in Table II.

Table I. Crystal Data and Experimental Details for [Ir(COD)(CO)$_2$L]ClO$_4$·CH$_2$Cl$_2$ (1; L = PPh$_3$ (a), AsPh$_3$ (b))

	1a	**1b**
formula	$C_{29}H_{29}Cl_3IrO_6P$	$C_{29}H_{29}Cl_3IrO_6As$
fw	803.08	847.03
cryst syst	orthorhombic	orthorhombic
space group	$Pna2_1$	$Pna2_1$
a, *b*, *c* (Å)	19.987 (4), 15.132 (3), 9.966 (2)	20.187 (1), 15.222 (3), 9.974 (5)
V (Å^3)	3014.3	3065.0
Z	4	4
d_{calcd} (g cm^{-3})	1.77	1.84
μ (cm^{-1})	47.7	57.1
cryst size (mm)	0.50 × 0.30 × 0.30	0.50 × 0.50 × 0.30
radiation	Mo Kα (λ = 0.701 73 Å)	Mo Kα (λ = 0.701 73 Å)
scan method	ω–2θ	ω–2θ
max 2θ (deg)	50	50
no. of rflns measd (total, unique)	2402, 2230	3059, 2849
no. of rflns obsd $F_o^2 > \sigma(F_o^2)$	1951	2460
no. of params	270	245
R^a	0.031	0.040
$R_w{}^b$	0.036	0.047

[a] $R = \sum(||F_o| - |F_c||)/|F_o|$. [b] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Collection and Refinement of X-ray Data for 1b. A pale red crystal of dimensions 0.50 × 0.50 × 0.30 mm was used. The lattice constants were determined for 23 intense reflections having $6 < \theta < 12°$. Crystal parameters and information for data collection and refinement are given in Table I. No absorption correction was made. A total of 3059 reflections were collected, of which 2849 were unique. Relative transmission coefficients ranged from 55.21 to 99.98 on *I*. Using 286 reflections (minimum *E* value of 1.20) and 8930 relationships, a total of 28 phase sets were produced. A total of two atoms were located from an *E*-map prepared from the phase set. All structural analyses were done similarly as for **1a**, except that the oxygen atoms of ClO_4^- and the carbon atom of CH_2Cl_2 were refined isotropically. The final positional parameters and isotropic equivalents of anisotropic thermal parameters for **1b** are given in Table II.

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(15) Iridium(I) complexes of $AsPh_3$ were prepared in a manner similar to that described for the PPh_3 analogues in refs 13 and 14.

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Table II. Non-Hydrogen Atom Positional and Equivalent Thermal Parameters for $[Ir(CO)(CO)_2(L)]ClO_4{\cdot}CH_2Cl_2$ (1; L = PPh_3 (a), $AsPh_3$ (b)) with Esd's in Parentheses[a]

	x	*y*	*z*	*B* (Å²)		*x*	*y*	*z*	*B* (Å²)
				Compound **1a**					
Ir	0.70522(1)	0.25389(2)	0.909	2.741(6)	C21	0.8253(4)	0.1910(5)	0.6815(9)	2.5(2)*
O1	0.6995(3)	0.4183(5)	0.7379(8)	5.4(2)	C22	0.8817(5)	0.1412(6)	0.648(1)	3.8(2)*
O2	0.6616(4)	0.0897(5)	0.7476(9)	7.4(2)	C23	0.8874(5)	0.1064(6)	0.517(1)	4.7(2)*
C1	0.7020(4)	0.3574(6)	0.802(1)	3.5(2)	C24	0.8369(5)	0.1186(6)	0.426(1)	5.2(2)*
C2	0.6760(5)	0.1511(7)	0.803(1)	4.7(3)	C25	0.7828(5)	0.1668(7)	0.457(1)	4.8(2)*
C3	0.7402(4)	0.2755(6)	1.1196(9)	3.1(2)	C26	0.7767(5)	0.2050(6)	0.584(1)	4.0(2)*
C4	0.7042(5)	0.3506(7)	1.191(1)	4.5(3)	C31	0.8656(4)	0.3381(5)	0.8494(9)	2.6(2)*
C5	0.6298(5)	0.3564(7)	1.153(1)	5.4(3)	C32	0.8428(4)	0.4109(5)	0.925(1)	3.8(2)*
C6	0.6147(5)	0.3280(7)	1.012(1)	4.3(2)	C33	0.8832(4)	0.4879(5)	0.932(1)	3.8(2)*
C7	0.5935(6)	0.2439(7)	0.980(1)	4.8(2)	C34	0.9423(5)	0.4907(6)	0.869(1)	3.9(2)*
C8	0.5893(5)	0.1662(7)	1.080(1)	5.4(3)	C35	0.9648(5)	0.4180(6)	0.792(1)	3.9(2)*
C9	0.6502(5)	0.1561(7)	1.169(1)	5.0(3)	C36	0.9260(4)	0.3419(6)	0.786(1)	3.2(2)*
C10	0.7149(5)	0.1877(7)	1.110(1)	4.0(2)	Cl3	0.5633(1)	0.2617(1)	0.5310(3)	3.77(6)
P	0.8165(1)	0.2361(1)	0.8434(3)	2.53(5)	O3	0.5485(4)	0.3081(6)	0.6504(9)	6.3(2)
C11	0.8623(4)	0.1592(5)	0.9530(9)	2.8(2)*	O4	0.5261(5)	0.2963(8)	0.423(1)	10.6(3)
C12	0.8512(4)	0.0685(5)	0.940(1)	3.9(2)*	O5	0.6322(4)	0.2728(5)	0.500(1)	6.8(2)
C13	0.8863(5)	0.0091(7)	1.018(1)	4.9(2)*	O6	0.5482(5)	0.1738(6)	0.552(1)	11.5(3)
C14	0.9326(5)	0.0373(7)	1.105(1)	5.2(3)*	Cl1	0.5988(2)	−0.1127(2)	0.7679(4)	6.55(8)
C15	0.9456(5)	0.1266(7)	1.122(1)	4.8(2)*	Cl2	0.6781(2)	−0.0705(2)	1.0013(4)	7.59(9)
C16	0.9107(4)	0.1899(6)	1.046(1)	3.4(2)*	C40	0.3907(6)	0.1293(8)	0.445(1)	6.4(3)
				Compound **1b**					
Ir	0.70097(2)	0.24463(3)	0.894	2.959(7)	C21	0.8265(6)	0.3118(7)	1.149(1)	3.2(2)*
O1	0.6975(4)	0.0832(6)	1.087(1)	5.5(2)	C22	0.8831(6)	0.3575(8)	1.181(1)	3.9(3)*
O2	0.6584(5)	0.4058(6)	1.067(1)	7.6(3)	C23	0.8872(7)	0.3905(9)	1.310(2)	5.5(3)*
C1	0.6984(5)	0.1432(8)	1.021(2)	4.2(3)	C24	0.8359(6)	0.3858(8)	1.403(2)	5.5(3)*
C2	0.6717(6)	0.3447(8)	1.011(1)	4.3(3)	C25	0.7808(7)	0.3369(9)	1.373(2)	5.3(3)*
C3	0.7369(6)	0.2241(8)	0.699(1)	3.5(3)	C26	0.7761(6)	0.3009(8)	1.240(1)	3.8(2)*
C4	0.7047(6)	0.1508(9)	0.627(1)	4.8(3)	C31	0.8669(5)	0.1573(6)	0.969(1)	2.9(2)*
C5	0.6317(7)	0.1403(9)	0.660(1)	5.5(4)	C32	0.8441(5)	0.0861(7)	0.869(2)	4.1(2)*
C6	0.6160(6)	0.1693(9)	0.806(1)	4.7(3)	C33	0.8835(6)	0.0104(7)	0.887(2)	4.2(2)*
C7	0.5931(6)	0.2532(9)	0.841(2)	5.2(3)	C34	0.9419(6)	0.0058(8)	0.948(1)	4.4(3)*
C8	0.5859(6)	0.3296(9)	0.739(2)	5.7(4)	C35	0.9661(6)	0.0801(9)	1.027(2)	4.7(3)*
C9	0.6480(6)	0.341(1)	0.647(1)	5.0(3)	C36	0.9291(6)	0.1543(8)	1.035(1)	3.9(3)*
C10	0.7128(6)	0.3110(9)	0.711(1)	3.9(3)	Cl3	0.0621(2)	0.2600(2)	0.2837(4)	3.66(7)
P	0.81610(6)	0.26447(7)	0.9634(1)	2.71(2)	O3	0.1307(6)	0.2687(6)	0.315(1)	6.9(3)*
C11	0.8657(5)	0.3462(7)	0.861(1)	2.9(2)*	O4	0.0469(5)	0.3085(7)	0.164(1)	6.4(3)*
C12	0.8560(6)	0.4341(7)	0.877(1)	4.3(3)*	O5	0.0285(7)	0.2970(9)	0.391(2)	10.5(4)*
C13	0.8928(7)	0.4930(9)	0.800(2)	5.4(3)*	O6	0.0449(6)	0.1734(9)	0.272(2)	9.3(4)*
C14	0.9375(7)	0.4632(9)	0.712(2)	5.3(3)*	Cl1	0.3933(2)	−0.3869(3)	0.5490(5)	6.8(1)
C15	0.9477(6)	0.3777(9)	0.694(2)	4.9(3)*	Cl2	0.3220(2)	−0.4285(3)	0.3143(6)	8.4(1)
C16	0.9135(6)	0.3147(8)	0.769(1)	3.9(3)*	C40	0.3886(8)	0.365(1)	0.382(2)	7.7(4)*

[a] Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Results and Discussion

Reactions in Solution. Reactions of iridium(I) complexes **3** and **4** with CO (1 atm) have been attempted in order to synthesize Ir^{I}–(COD)(CO) complexes in methylene chloride at 25 °C, without success. Complex **3a** reacts with CO to give $[Ir(COD)(CO)_2(PPh_3)]ClO_4$ (**1a**) in solution. However, **1a** rapidly reacts with CO in solution to produce unknown Ir–CO complex(es) and free COD, which is the reason that **1a** has never been isolated in good purity at 25 °C. It is known that a nitrile in iridium(I) complexes is readily replaced by CO and PR_3.[13,17] However, COD in the related rhodium(I)–COD complexes $[Rh(COD)(PPh_3)(L')]^+$ (L′ = nitriles,[18] other nitrogen-donor ligands[19]) and $[Rh(COD)(RCN)_2]^+$ [20] is replaced rather than nitrogen base ligands to give $[Rh(PPh_3)(L')(CO)_2]^+$ and $[Rh(RCN)_2(CO)_2]^+$, respectively. Complex **1a** can be obtained in high yield by the reaction of **3a** with CO at low temperature (−20 °C).

The reaction of **4a** with CO in solution produces the known complex $[Ir(CO)_3(PPh_3)_2]ClO_4$ (**5**)[21] even at −30 °C, according to eq 1, within 5 min. Reactions of

$$\underset{\textbf{4a}}{[Ir(COD)(PPh_3)_2]ClO_4} + 3CO \xrightarrow{CH_2Cl_2} \underset{\textbf{5}}{[Ir(CO)_3(PPh_3)_2]ClO_4} + COD \quad (1)$$

triphenylarsine complexes **3b** and **4b** with CO respectively produce oily unknown iridium complex(es) which seem to contain coordinated COD, CO, and $AsPh_3$ on the basis of ^1H NMR and IR spectral data.

Reactions in the Solid State. Reactions of iridium(I) complexes **3** and **4** with CO (P_{CO} = 1 atm) were carried out in the solid state at 25 °C. The complexes **3a** and **3b** react with CO to give **1a** and **1b** quantitatively which do not further react with CO in the solid state for 2 weeks at room temperature (eq 2). Recrystallization of the com-

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[17] (a) Burrell, A. K.; Roper, W. R. *Organometallics* **1990**, *9*, 1905. (b) Basato, M.; Longato, B.; Morandini, F.; Bresadola, S. *Inorg. Chem.* **1984**, *23*, 3972. (c) Reed, C. A.; Roper, W. R. *J. Chem. Soc., Dalton Trans.* **1973**, 1365.

[18] Unpublished results.

[19] Uson, R.; Oro, L. A.; Claver, C.; Garralda, M. A. *J. Organomet. Chem.* **1976**, *105*, 365.

[20] Uson, R.; Oro, L. A.; Artigas, J.; Sariego, R. *J. Organomet. Chem.* **1979**, *179*, 65.

[21] Day, V. W.; Klemperer, W. G.; Main, D. J. *Inorg. Chem.* **1990**, *29*, 2345.

$$\underset{\mathbf{3}}{[\mathrm{Ir(COD)(L)(PhCN)}]\mathrm{ClO_4}} + 2\mathrm{CO} \xrightarrow[-\mathrm{PhCN}]{25\ ^\circ\mathrm{C},\ 24\ \mathrm{h}} \underset{\mathbf{1}}{[\mathrm{Ir(COD)(L)(CO)_2}]\mathrm{ClO_4}} \quad (2)$$

$$\mathrm{L} = \mathrm{PPh_3}\ (\mathbf{a}),\ \mathrm{AsPh_3}\ (\mathbf{b})$$

plexes **1a** and **1b** in methylene chloride/*n*-hexane gives red **1a**·CH_2Cl_2 and pale red **1b**·CH_2Cl_2 crystals, respectively, which are stable in both solution and the solid state under nitrogen. Spectral data (^{1}H NMR, ^{13}C NMR, and IR) for **1a**·CH_2Cl_2 are practically identical with those for **1b**·CH_2Cl_2 (see Experimental Section). The X-ray analysis shows that the crystal structures of **1a**·CH_2Cl_2 and **1b**·CH_2Cl_2 are much alike, with some minor differences in bond angles and distances (vide infra). Selected bond distances and bond angles are given in Table III. ORTEP drawings of the cations in **1a**·CH_2Cl_2 and **1b**·CH_2Cl_2 are given in Figures 1 and 2, showing the same atomic numbering for both compounds.

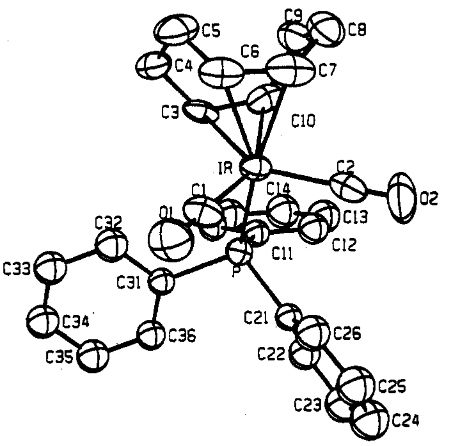

Figure 1. ORTEP drawing of the cation of **1a**, $[\mathrm{Ir(COD)(CO)_2(PPh_3)}]^+$, showing the labeling scheme with 50% thermal ellipsoids. The counteranion and CH_2Cl_2 of solvation are omitted for simplicity.

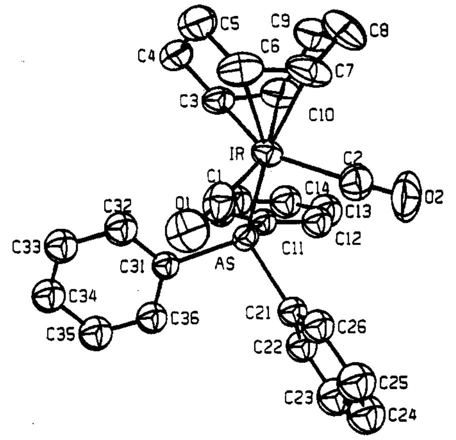

Figure 2. ORTEP drawing of the cation of **1b**, $[\mathrm{Ir(COD)(CO)_2(AsPh_3)}]^+$, showing the labeling scheme with 50% thermal ellipsoids. The counteranion and CH_2Cl_2 of solvation are omitted for simplicity.

Crystal structures of the 18-e$^-$ iridium(I) complexes **1a**·CH_2Cl_2 and **1b**·CH_2Cl_2 are similar to that of the anionic iridium(I)–COD complex $[\mathrm{Ir(COD)(P_3O_9)}]^{2-}$, where two olefinic groups of COD and three oxygen atoms of $P_3O_9{}^{3-}$ form a square-pyramidal geometry around the iridium(I) atom.[19] The average bond distances between iridium and carbon atoms of the olefinic groups of COD are significantly longer in **1a**·CH_2Cl_2 (2.30 Å) than in **1b**·CH_2Cl_2 (2.17 Å) and other Ir$^{\mathrm{I}}$–COD complexes (ca. 2.11–2.16 Å),[21,22] while all the C=C (COD) bond distances observed for **1a**·CH_2Cl_2 and **1b**·CH_2Cl_2 are very close to each other (1.38–1.41 Å). It is noticed in Table III that one Ir–C(CO) bond distance (Ir–C1, 1.90 Å) of **1a**·CH_2Cl_2 is somewhat shorter than the other one (Ir–C2, 1.97 Å) and those (1.99 and 2.00 Å) of **1b**·CH_2Cl_2, while all the C–O(CO) distances observed for **1a**·CH_2Cl_2 and **1b**·CH_2Cl_2 are very close to each other (1.12–1.13 Å). No interaction was observed between the iridium atom and methylene chloride in **1a**·CH_2Cl_2 and **1b**·CH_2Cl_2: the distance between the iridium atom and the CH_2Cl_2 molecule is too long to show any interaction, whereas CH_2Cl_2 is close to the counteranion $ClO_4{}^-$.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[\mathrm{Ir(COD)(CO)_2(L)}]\mathrm{ClO_4}$ (1; L = PPh_3 (a), $AsPh_3$ (b)) with Esd's in Parentheses

	1a	**1b**		**1a**	**1b**
		Bond Distances (Å)			
Ir–C1	1.90(1)	1.99(1)	C3–C4	1.52(1)	1.48(2)
Ir–C2	1.97(1)	2.00(1)	C3–C10	1.43(1)	1.41(2)
Ir–C3	2.235(9)	2.10(1)	C4–C5	1.54(1)	1.52(2)
Ir–C6	2.36(1)	2.24(1)	C5–C6	1.51(2)	1.55(2)
Ir–C7	2.35(1)	2.25(1)	C6–C7	1.38(1)	1.40(2)
Ir–C10	2.24(1)	2.10(1)	C7–C8	1.55(2)	1.55(2)
O1–C1	1.12(1)	1.13(2)	C8–C9	1.52(2)	1.56(2)
O2–C2	1.12(1)	1.12(2)	C9–C10	1.50(1)	1.53(2)
Ir–L	2.321(3)	2.442(1)			
		Bond Angles (Å)			
L–Ir–C1	88.9(3)	86.7(3)	C2–Ir–C6	112.4(4)	113.0(5)
L–Ir–C2	93.0(3)	91.3(4)	C2–Ir–C7	80.2(4)	79.0(5)
L–Ir–C3	87.8(2)	87.2(3)	C2–Ir–C10	98.8(4)	100.0(5)
L–Ir–C6	154.5(2)	154.3(3)	C3–Ir–C6	76.4(3)	79.8(5)
L–Ir–C7	169.4(3)	169.2(4)	C3–Ir–C7	91.5(4)	97.1(5)
L–Ir–C10	95.6(2)	94.4(3)	C3–Ir–C10	37.1(3)	39.4(5)
C1–Ir–C2	109.8(4)	102.3(5)	C6–Ir–C7	34.0(3)	36.4(5)
C1–Ir–C3	114.7(4)	118.6(5)	C6–Ir–C10	83.9(4)	89.5(5)
C1–Ir–C6	80.0(4)	80.4(5)	C7–Ir–C10	77.7(4)	82.9(5)
C1–Ir–C7	101.0(4)	99.8(5)	Ir–C1–O1	179.2(8)	177.0(1)
C1–Ir–C10	150.8(4)	157.7(5)	Ir–C2–O2	175.8(9)	173.0(1)
C2–Ir–C3	135.5(4)	138.8(5)			

Compounds **4a** and **4b** readily react with CO ($P_{\mathrm{CO}} = 1$ atm) in the solid state to give **2a** and **2b** within 30 min at 25 °C (eq 3). The carbonyl iridium(I) complex **2a** further

$$\underset{\mathbf{4}}{[\mathrm{Ir(COD)(L)_2}]\mathrm{ClO_4}} + \mathrm{CO} \xrightarrow{25\ ^\circ\mathrm{C},\ <30\ \mathrm{min}} \underset{\mathbf{2}}{[\mathrm{Ir(COD)(CO)(L)_2}]\mathrm{ClO_4}} \quad (3)$$

$$\mathrm{L} = \mathrm{PPh_3}\ (\mathbf{a}),\ \mathrm{AsPh_3}\ (\mathbf{b})$$

$$\underset{\mathbf{2a}}{[\mathrm{Ir(COD)(CO)(PPh_3)_2}]\mathrm{ClO_4}} + 2\mathrm{CO} \xrightarrow[-\mathrm{COD}]{25\ ^\circ\mathrm{C},\ 24\ \mathrm{h}} \underset{\mathbf{5}}{[\mathrm{Ir(PPh_3)_2(CO)_3}]\mathrm{ClO_4}} \quad (4)$$

reacts with CO to produce **5** (eq 4). However, the reaction is slow enough in the solid state to allow **2a** to be isolated almost quantitatively. Complex **2a** is somewhat stable in the solid state, while the beige solid **2a** turns immediately

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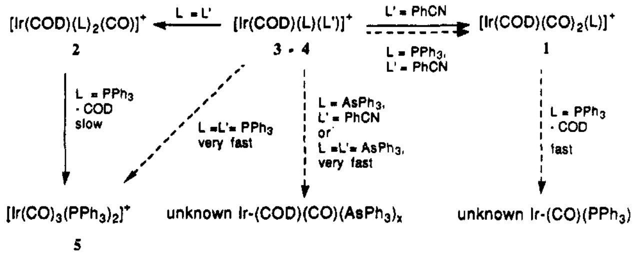
(22) (a) van der Zeijden, A. H.; van Koten, G.; Luijk, R.; Nordemann, R. A.; Spek, A. L. *Organometallics* **1988**, *7*, 1549. (b) Sielish, T.; Cowie, M. *Organometallics* **1988**, *7*, 707. (c) Beveridge, K. A.; Bushnell, G. W.; Stobart, S. R.; Atwood, J. L.; Zaworotko, M. J. *Organometallics* **1983**, *2*, 1447.

Scheme I[a]



[a] Conditions: temperature 25 °C; P_{CO} = 1 atm. L = PPh_3 (**a**), $AsPh_3$ (**b**). Solid-state reactions are designated by a solid arrow and solution-state reactions with a dashed arrow.

red in chloroform solution under nitrogen at 25 °C; this reaction is currently under investigation. The arsine analogue **2b** does not react with CO under the same experimental conditions.

Comparison of Reactions in the Solid State with Those in Solution. Scheme I shows the reactions of complexes **3** and **4** with CO (P_{CO} = 1 atm) in both solution and the solid state. Complex **1a** does not react with CO for 2 weeks in the solid state, while **1a** further reacts with CO (P_{CO} = 1 atm) in methylene chloride solution to give unknown Ir complex(es) and free COD within 15 min at room temperature. Complex **2a** could be obtained by the reaction of **4a** at room temperature and further reacts with CO in the solid state to give **5**. Complex **5** is produced by the reaction of **4a** with CO (P_{CO} = 1 atm) in solution even at −30 °C within 5 min. Complexes **3b** and **4b** react with CO in the solid state to give **1b** and **2b**, while the complexes react with CO in solution to give an unknown Ir complex(es) containing COD, CO, and $AsPh_3$ on the basis of IR and ^1H NMR spectral data.

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Supplementary Material Available: Tables of complete bond distances and angles, anisotropic displacement parameters (U's), least-squares planes, and positional parameters of hydrogen atoms for **1a**·CH_2Cl_2 and **1b**·CH_2Cl_2 (17 pages). Ordering information is given on any current masthead page.

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