Organometallics 1982, *1*, 1361–1366

Iridium Complexes of Some Halocarbons and the Crystal and Molecular Structure of *cis,trans*-[$IrH_2(o\text{-}C_6H_4I_2)(PPh_3)_2]BF_4$

Robert H. Crabtree,* J. W. Faller,* Michelle F. Mellea, and Jennifer M. Quirk

Department of Chemistry, Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06511

Received May 19, 1982

cis,cis,trans-[$IrH_2(Me_2CO)_2L_2$]BF_4 (L = PPh_3) reacts with various halocarbons L′ which displace Me_2CO to give *cis,trans*-[$IrH_2(L')L_2$] (L′ = *o*-diiodobenzene and *o*-bromoiodobenzene). The crystal structure of the $C_6H_4I_2$ complex was determined by X-ray methods. This complex crystallizes in the space group $P2_1/n$ with a = 13.309 (4) Å, b = 19.144 (4) Å, c = 16.317 (7) Å, β = 109.85 (3)°, and Z = 4. Full-matrix least-squares refinement using anisotropic thermal parameters for the iridium, phosphorus, iodine, and fluorine atoms and isotropic thermal parameters for the remaining atoms converged to the final residuals R_1 = 0.047 and R_2 = 0.050. The L′ ligand was found to chelate to iridium via the halogen groups. Other more weakly binding ligands such as C_6H_5I and RI (R = Me, Et, *i*-Pr) do not displace Me_2CO, but analogous complexes can be obtained by hydrogenating [$Ir(cod)L_2$]BF_4 (cod = 1,5-cyclooctadiene) in the presence of the halocarbon. These have been detected by ^1H NMR and in some cases isolated. Some analogues were obtained for L = $PMePh_2$. The halo ligands were displaced by MeCN and displaced or partially displaced by EtOH (100 molar equiv).

Introduction

R_3P and R_2S have been used as ligands in transition-metal chemistry since the nineteenth century. They stabilize a wide series of complexes. R_3P complexes are also particularly important in catalysis.[1] The group 7 alkyls and aryls, RX (X = Cl, Br or I), are almost unknown as ligands. The only cases seem to be [$RhClIMe(MeI)(PPh_3)_2$][2] and the MeI adducts of $GeCl_4$.[3]

We were interested in the possibility of obtaining RX complexes (X = halogen) of iridium for a number of reasons. First, RX complexes seem likely to be intermediates in oxidative addition of RX to transition metals.[4] This might seem to militate against the likelihood of obtaining stable, isolable RX complexes since they might be expected to decompose via oxidative addition. An iridium-based homogeneous hydrogenation system[5] we have studied was, surprisingly, entirely resistant to oxidation by RX, so that in this system, at least the oxidative addition pathway for the decomposition of any RX complexes was suppressed. In our iridium-based alkane activation[6] and catalytic hydrogenation[5] systems, chlorinated solvents, particularly CH_2Cl_2, are preferred. We wondered whether these might chelate to Ir via the halo groups. Evidence for competitive binding of PhCl to iridium was obtained when we found that this halocarbon lowered the rate of olefin hydrogenation as efficiently as does *i*-PrOH, which is known to bind to Ir to give an isolable solvent complex,[7] but that (η^6-PhCl) complexes did not seem to be formed.

Results and Discussion

In order to maximize our chances of obtaining isolable complexes with the weakly binding halocarbons RX, we studied iodo compounds, where we hoped the binding would be strongest, since iodine is the least electronegative and the softest of the halogens. For a suitable metal complex, we chose the iridium solvent complexes *cis,cis,trans*-[$IrH_2S_2L_2$]BF_4 (**1**, S = Me_2CO; L = PPh_3) that we had already studied in detail.[6,7] These lose the S groups very readily to expose two cis-binding sites. A chelating diiodide was therefore indicated. We had already shown[8] that the organic C═O group binds to **1** via O and that the binding is stronger when C═C or aromatic functionality is in conjugation with the donor group. We ascribe this to a lowering of the C═O π^* orbitals allowing more extensive M–O dπ–pπ bonding. When this idea is applied to the case at hand, *o*-diiodobenzene seemed best suited for a first attempt.

$C_6H_4I_2$ reacts readily with [$IrH_2S_2L_2$]BF_4, **1**, at 25 °C in CH_2Cl_2 to give [$IrH_2(C_6H_4I_2)(PPh_3)_2$]$BF_4$, **2**. The ^1H NMR spectrum of the product shows a triplet assigned to Ir–H at δ −16.46 with a coupling, $^2J_{PH}$ = 13 Hz, appropriate[6,7] for a mutually cis arrangement of H and L, as in **1** itself. $C_6H_4I_2$ resonances were apparently obscured by those due to L. When **1** is treated with $C_6H_4I_2$ in an NMR tube, the spectrum of **1** is immediately and cleanly replaced by that of **2**, after a slight excess of $C_6H_4I_2$ has been added. No extraneous resonances, apart from that due to free acetone (δ 2.07), were observed.

Unchanged $C_6H_4I_2$ (GC) was displaced by bipyridyl to give **1** (S_2 = bpy) and by MeCN to give **1** (S = MeCN;[7] ^1H NMR). NMR studies also showed that neither Me_2CO nor THF (100 molar equiv) could displace $C_6H_4I_2$ but that EtOH was competitive with $C_6H_4I_2$, an equilibrium mixture of **1** and **2** being observed. This suggests that in spite of chelation, the aryl iodide is only weakly bound. The mutual displacement order of the added ligands has previously been determined[7] as H_2O < THF < Me_2CO < EtOH < MeCN < bpy.

2 was thermally stable and in particular did not undergo oxidative addition, but it does undergo some of the reactions of **1**. For example, **2** (L = PPh_3 or $PMePh_2$) reacts (CH_2Cl_2, 40 °C, 30 min) with styrene to give [(η^6-PhEt)IrL_2]BF_4[9] and with cyclopentene to give [(π-Cp)$IrHL_2$]BF_4[6] as does **1** (S = Me_2CO). In contrast to **1**, **2** fails to react with cyclopentane in the presence of *tert*-butylethylene (($CH_2Cl)_2$, 80 °C, 18 h). The $PMePh_2$ analogue of **1** (S = Me_2CO) also reacts with $C_6H_4I_2$ to give an analogous product.

---

[1] Parshall, G. W. "Homogenous Catalysis"; Wiley: New York, 1980.

[2] Lawson, D. N.; Osborn, J. A.; Wilkinson, G. W. *J. Chem. Soc. A* **1966**, 1733.

[3] Brown, H. C.; Eddy, L. P.; Wong, R. *J. Am. Chem. Soc.* **1953**, *75*, 6275.

[4] Vaska, L. *Acc. Chem. Res.* **1968**, *1*, 335.

[5] Crabtree, R. H. *Acc. Chem. Res.* **1979**, *12*, 331.

[6] Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107.

[7] Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E., *J. Am. Chem. Soc.*, in press.

[8] Suggs, J. W.; Cox, S. D.; Crabtree, R. H.; Quirk, J. M. *Tetrahedron Lett.* **1981**, *22*, 303.

[9] Crabtree, R. H.; Mellea, M. F.; Quirk, J. M. *J. Chem. Soc., Chem.Commun.* **1981**, 1217.

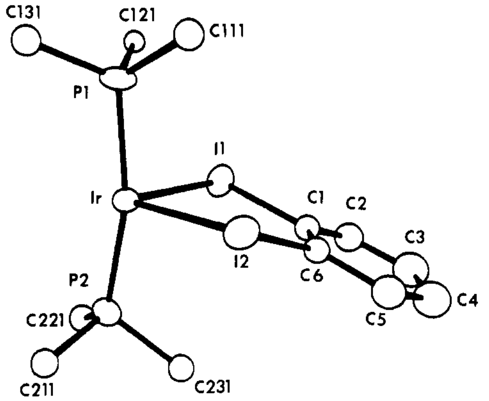

Figure 1. An ORTEP diagram of the core of the $[IrH_2(C_6H_4I_2)(PPh_3)_2]^+$ cation. The hydrogen ligands were not located, and carbon atoms of the C_6H_5 groups other than the one directly bound to P have been omitted for clarity.

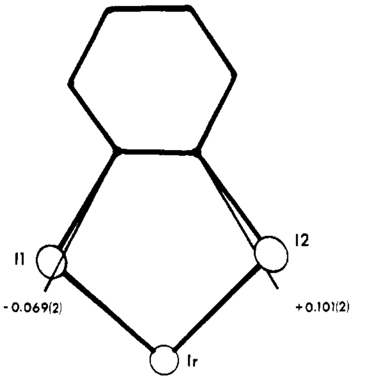

Figure 2. Distortions in the $C_6H_4I_2$ ligand. The thin lines cutting I(1) and I(2) represent idealized C–I bond vectors and lie in the C_6 plane with $C_xC_{x+1}I = IC_{x+1}C_{x+2}$. The figures show the vertical distances (Å) of I(1) and I(2) above or below the C_6 plane.

Table I. Experimental Data for X-ray Diffraction Study of $Ir(I_2C_6H_4)[P(C_6H_5)_3]H_2BF_4$

(A) Crystal Parameters at 26 (2) °C

space group $P2_1/n$, No. 14

a = 13.309 (4) Å	V = 3910 (5) $Å^3$
b = 19.144 (4) Å	Z = 4
c = 16.317 (7)	mol wt 1135.52
β = 109.85 (3)°	ρ_{calcd} 1.929 g/cm^3

(B) Measurement of Intensity Data

radiation	Mo Kα, 0.710 73 Å
monochromator	graphite
detector aperture	horizontal, $A + B \tan \theta$ (A = 3.0 mm, B = 1.0 mm); vertical, 4.0 mm
reflections measured	$+h,+k,\pm l$
2θ(max)	46°
scan type	moving crystal–stationary counter
ω scan rate, deg/min	max, 10; min, 1.25
ω scan width, deg	0.80
background	one-fourth additional scan at each end of scan
std reflections	three measured after each 90 min, showing only random fluctuations of ± 2%.
reflections measd	5989 including absences
data used ($F^2 > 3\sigma(F^2)$)	2235

(C) Treatment of Data

absorption coeff (μ, cm^{-1})	53.409
transmission coeff (max, min)	0.69, 0.41
grid	8 × 8 × 8
p factor	0.02
final residuals (R_1, R_2)	0.047, 0.050
esd of unit weight	1.78

The Structural Results. A definitive characterization of **2** (L = PPh_3) required a crystal structure determination. The complex was recrystallized from a CH_2Cl_2/Et_2O bilayer to give suitable material. The crystallographic data are given in Tables I–IV and VI–IX (supplementary material). Diagrams of the structure are shown in Figures 1 and 2.

The structure consists of discrete BF_4 anions and $[IrH_2(C_6H_4I_2)(PPh_3)_2]^+$ cations with no unusually close contacts and reasonable distances and angles. The most interesting feature is the characterization for the first time of a covalent bond between a neutral halogen atom of a halocarbon and a transition metal. The bond distances 2.726 (2) and 2.745 (1) Å are in the same range as the corresponding bonds to iodide in $[Ir(p\text{-}MeOC_6H_3NNH)HI(PPh_3)_2]$[10] (2.786 Å) and $[Ir(C_5Me_5)(\mu\text{-}I)I]_2$[11] (Ir–I = 2.694 Å; Ir–(μ-I) = 2.710 Å) and must correspond to full covalent bonds. Since RI may be a rather poor σ donor but a more strong π acceptor compared with R_3P or R_2S, the iridium site is appropriately matched in being soft (it can bind thioethers[12] or CO[13]) but also quite hard (σ Lewis acid; it can bind H_2O[6]). **1** also contains very labile S ligands, and we have used an essentially noncoordinating solvent. The comparative rarity of this combination of circumstances may help explain why RX complexes are so rare. A second feature of interest is the angle (21°) that the ligand C_6 plane makes with the IrI_2 plane. A possible reason is that this angle best accommodates the preferred interbond angle at I, which one would expect to be less than 109° on VESPR[14] considerations. The CIIr angles (99.9 (5) and 101.8 (5)°) seem reasonable considering that excessive steric interference between the halocarbon aromatic group and the PPh_3 that might result from a further decrease.

The I–I distance (3.72 Å) is much shorter than the sum of the van der Waals radii (4.3 Å). Consequently, the iodine atoms are slightly displaced from their ideal positions. Figure 2 shows the splaying out of I(1) and I(2) in both the C_6 plane and the normal to it (see figure caption). The resulting bite angle of the chelate ligand (I(1)–Ir–I(2) = 85.65 (4)°) is nearly ideal for an octahedral configuration.

A further distortion can be seen in Figure 1: P(1) and P(2) are bent (P(1)IrP(2) = 166.5 (2)°) away from the halocarbon toward the positions that must be occupied by the hydrogen ligands. The phenyl groups on P(1) are staggered with respect to those on P(2).

Analogous Complexes. We wondered whether the iodine donor atom was required for binding or whether bromine would serve. o-Bromoiodobenzene reacts rapidly with **1** to give an isolable complex $[IrH_2(C_6H_4BrI)L_2]BF_4$. The ^1H NMR spectrum of the product at 220 K shows two IrH resonances at δ –16.6 and at δ 20.0 (Table V). Each is a doublet of triplets of equal intensity. The smaller coupling (6.5 Hz) can be ascribed to $^2J_{HH}$ because irradiation at each Ir–H frequency leads to the loss only of the $^2J_{HH}$ splitting of the other resonances. This shows that both resonances must arise from a single complex. Warming the sample leads to gradual broadening, and by 290 K, the two Ir–H resonances have collapsed, presumably

---

[10] Bellon, P. L.; Demartin, E.; Manassero, M.; Sansoni, M.; Caglio, G. *J. Organomet. Chem.* **1978**, *157*, 209.

[11] Churchill, M. R.; Julis, S. A. *Inorg. Chem.* **1979**, *18*, 1215.

[12] Crabtree, R. H.; Davis, M., unpublished results (1980).

[13] Church, M. J.; Mays, M. J.; Simpson, R. N. F.; Stefanini, F. P. *J. Chem. Soc. A* **1970**, 2909, 3000.

[14] Gillespie, R. J. *J. Chem. Educ.* **1974**, *51*, 367.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations For $\{Ir(I_2C_6H_4)[P(C_6H_5)_3]H_2\}BF_4$

atom	*x/a*	*y/b*	*z/c*	*B*, Å^2	atom	*x/a*	*y/b*	*z/c*	*B*, Å^2
Ir	0.00387 (7)	0.24119 (5)	0.16836 (6)	*a*	C(134)	0.043 (2)	0.439 (1)	−0.113 (1)	3.0 (5)
I(1)	0.0583 (1)	0.10372 (9)	0.19555 (10)	*a*	C(135)	0.132 (2)	0.397 (1)	−0.100 (1)	2.9 (5)
I(2)	0.1549 (1)	0.26313 (9)	0.32942 (9)	*a*	C(136)	0.158 (2)	0.342 (1)	−0.039 (1)	2.0 (5)
P(1)	0.1172 (4)	0.2556 (4)	0.0872 (4)	*a*	C(211)	−0.183 (2)	0.327 (1)	0.234 (1)	2.2 (5)
P(2)	−0.1392 (4)	0.2386 (4)	0.2208 (4)	*a*	C(212)	−0.300 (2)	0.342 (1)	0.209 (1)	2.8 (5)
C(1)	0.139 (2)	0.101 (1)	0.335 (1)	2.1 (5)	C(213)	−0.334 (2)	0.410 (1)	0.222 (2)	4.8 (7)
C(2)	0.152 (2)	0.033 (1)	0.370 (1)	2.9 (6)	C(214)	−0.252 (2)	0.461 (1)	0.253 (2)	4.7 (7)
C(3)	0.205 (2)	0.028 (1)	0.461 (2)	4.0 (6)	C(215)	−0.145 (2)	0.446 (1)	0.275 (1)	3.4 (6)
C(4)	0.233 (2)	0.088 (1)	0.511 (1)	3.7 (6)	C(216)	−0.111 (2)	0.379 (1)	0.261 (1)	2.7 (5)
C(5)	0.219 (2)	0.154 (1)	0.475 (1)	2.9 (6)	C(221)	−0.256 (2)	0.185 (1)	0.161 (1)	2.7 (5)
C(6)	0.169 (2)	0.161 (1)	0.380 (1)	1.9 (5)	C(222)	−0.259 (2)	0.151 (1)	0.084 (2)	3.6 (6)
C(111)	0.255 (1)	0.267 (1)	0.154 (1)	2.3 (5)	C(223)	−0.352 (2)	0.109 (1)	0.037 (1)	3.7 (6)
C(112)	0.294 (2)	0.337 (1)	0.179 (1)	3.5 (6)	C(224)	−0.432 (2)	0.098 (1)	0.073 (1)	3.5 (6)
C(113)	0.396 (2)	0.350 (1)	0.238 (2)	3.9 (6)	C(225)	−0.421 (2)	0.128 (1)	0.156 (1)	3.1 (6)
C(114)	0.461 (2)	0.292 (1)	0.279 (1)	2.8 (5)	C(226)	−0.337 (2)	0.173 (1)	0.196 (1)	3.5 (6)
C(115)	0.423 (2)	0.225 (1)	0.259 (2)	4.4 (7)	C(231)	−0.106 (2)	0.205 (1)	0.333 (1)	2.2 (5)
C(116)	0.319 (2)	0.209 (1)	0.194 (1)	3.0 (6)	C(232)	−0.099 (2)	0.129 (1)	0.351 (1)	3.2 (6)
C(121)	0.118 (2)	0.176 (1)	0.020 (1)	1.5 (5)	C(233)	−0.070 (2)	0.102 (1)	0.432 (1)	3.2 (5)
C(122)	0.029 (2)	0.137 (1)	−0.012 (1)	2.3 (5)	C(234)	−0.053 (2)	0.145 (1)	0.497 (2)	3.9 (6)
C(123)	0.028 (2)	0.075 (1)	−0.061 (1)	3.2 (6)	C(235)	−0.047 (2)	0.216 (1)	0.497 (2)	3.9 (6)
C(124)	0.124 (2)	0.055 (1)	−0.073 (2)	4.5 (7)	C(236)	−0.084 (2)	0.249 (1)	0.407 (1)	3.0 (5)
C(125)	0.218 (2)	0.096 (1)	−0.043 (2)	4.6 (7)	B	0.179 (2)	0.473 (2)	0.315 (2)	4.7 (8)
C(126)	0.215 (2)	0.158 (1)	0.004 (2)	3.6 (6)	F(1)	0.128 (1)	0.419 (1)	0.275 (2)	*a*
C(131)	0.084 (2)	0.329 (1)	0.007 (1)	2.4 (5)	F(2)	0.122 (1)	0.517 (1)	0.340 (1)	*a*
C(132)	−0.006 (2)	0.368 (1)	−0.005 (2)	4.4 (7)	F(3)	0.274 (2)	0.003 (1)	0.234 (1)	*a*
C(133)	−0.030 (2)	0.422 (1)	−0.069 (2)	3.9 (6)	F(4)	0.262 (2)	0.449 (1)	0.385 (1)	*a*

atom	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Ir	0.00342 (5)	0.00156 (3)	0.00316 (3)	−0.0001 (1)	0.00248 (6)	−0.00001 (8)
I(1)	0.00669 (12)	0.00174 (5)	0.00233 (7)	0.0003 (2)	0.0016 (1)	−0.0006 (1)
I(2)	0.00472 (9)	0.00208 (5)	0.00250 (6)	−0.0012 (1)	0.0023 (1)	−0.0007 (1)
P(1)	0.0042 (3)	0.0022 (2)	0.0042 (3)	−0.0009 (6)	0.0058 (4)	−0.0002 (5)
P(2)	0.0040 (4)	0.0016 (2)	0.0031 (3)	0.0000 (6)	0.0030 (5)	−0.0001 (5)
F(1)	0.013 (2)	0.0054 (8)	0.022 (2)	−0.006 (2)	0.013 (3)	−0.007 (2)
F(2)	0.014 (2)	0.0111 (10)	0.013 (1)	0.016 (2)	−0.001 (2)	−0.010 (2)
F(3)	0.025 (2)	0.0141 (13)	0.015 (2)	0.019 (3)	0.015 (3)	−0.008 (2)
F(4)	0.015 (2)	0.0141 (15)	0.008 (1)	0.011 (3)	0.003 (3)	0.002 (2)

[a] Anisotropic thermal parameters are listed in the second half of the table. The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B(1,1)h^2a^{*2} + B(2,2)k^2b^{*2} + B(3,3)l^2c^{*2} + B(1,2)hka^*b^* + B(1,3)hla^*c^* + B(2,3)klb^*c^*)]$. [b] Hydrogen atom positions were calculated and not refined. Isotropic thermal parameters of 5.0 Å^2 were used.

Table III. Selected Bond Lengths (Å) for $\{Ir(I_2C_6H_4)[P(C_6H_5)_3H_2\}BF_4$

Ir-I(1)	2.726 (2)	C(1)-C(2)	1.41 (2)
Ir-I(2)	2.745 (1)	C(2)-C(3)	1.42 (3)
Ir-P(1)	2.337 (4)	C(3)-C(4)	1.40 (3)
Ir-P(2)	2.339 (4)	C(4)-C(5)	1.37 (2)
I(1)-C(1)	2.17 (2)	C(5)-C(6)	1.48 (2)
I(2)-C(6)	2.10 (2)	C(6)-C(1)	1.35 (2)

Table IV. Selected Bond Angles (Deg) for $\{Ir(I_2C_6H_4)[P(C_6H_5)_3H_2\}BF_4$

I(1)-Ir-I(2)	85.65 (4)	C(6)-C(1)-C(2)	127 (2)
I(1)-Ir-P(1)	91.1 (2)	C(1)-C(2)-C(3)	116 (2)
I(1)-Ir-P(2)	97.1 (1)	C(2)-C(3)-C(4)	119 (2)
I(2)-Ir-P(1)	96.9 (1)	C(3)-C(4)-C(5)	123 (2)
I(2)-Ir-P(2)	94.3 (1)	C(4)-C(5)-C(6)	119 (2)
P(1)-Ir-P(2)	166.5 (2)	C(5)-C(6)-C(1)	116 (2)
Ir-I(1)-C(1)	101.8 (5)	Ir-P(1)-C(111)	112.9 (5)
Ir-I(2)-C(6)	99.9 (5)	Ir-P(1)-C(121)	111.7 (6)
I(1)-C(1)-C(2)	113 (1)	Ir-P(1)-C(131)	116.0 (6)
I(1)-C(1)-C(6)	120 (1)	Ir-P(2)-C(211)	110.8 (6)
I(2)-C(6)-C(1)	128 (1)	Ir-P(2)-C(221)	117.6 (6)
I(1)-C(6)-C(5)	117 (1)	Ir-P(2)-C(231)	114.9 (6)

to a single very broad peak. Experimental difficulties have prevented us observing the limiting high-temperature spectrum, but we do know that cooling the sample restores the original spectrum. The fluxionality responsible may involve competition between the halocarbon and water present in the solvent. RBr therefore seems to bind, but probably more weakly than does RI. ^1H NMR experiments show that 10 molar equiv of Me_2CO leads to competitive displacement of C_6H_4BrI, in contrast to the case of the corresponding diiodide. Me_2SO and bipyridyl also displace the C_6H_4BrI as expected.

We naturally wished to extend our studies to the more weakly binding halides. In doing so, we ran the risk of failing to observe binding because RX could not displace S from $[IrH_2S_2L_2]^+$ (**1**). One might be able to avoid this problem by starting not from **1** but from $[Ir(cod)L_2]^+$ (**3**, cod = 1,5-cyclooctadiene). In CH_2Cl_2, H_2 removes the cod as cyclooctane, and the ligand-deficient fragment $[IrH_xL_2]^+$ so formed dimerizes at once to $[Ir_2H_5L_4]^+$ unless trapped by a suitable ligand.[6]

To test this idea, we ran an in situ hydrogenation (1 h at 0 °C) of **3** in $CDCl_3$ containing C_6H_4BrI in an NMR tube. At 213 K, the characteristic resonances of the C_6H_4BrI complex were seen. Free cyclooctane (δ 1.46) was also detected. The same fluxional behavior was observed on warming.

o-Dibromobenzene, $C_6H_4Br_2$, also reacts with **1** at 220 K in an NMR experiment; various hydridic products were formed, none of which could be identified with certainty. Hydrogenation of **3** in the presence of $C_6H_4Br_2$ gave a product having an Ir–H resonance at δ −20.8 ($^2J_{PH}$ = 13.3 Hz) and a resonance we ascribe to coordinated $C_6H_4Br_2$ at δ 7.06. The $C_6H_4Br_2$ is displaced by EtOH. We have already noted[5,7] the sensitivity of the position of the Ir–H resonance in complexes of the type *cis,cis,trans*-$[IrH_2S_2L_2]^+$ to the nature of the trans-ligand S. Oxygen

Table V. ^{1}H NMR Data for the Complexes

complex[a]			^{1}H NMR data[c]		
RX	L	temp,[b] K	Ir–H	RX	synthetic method[d]
$C_6H_4I_2$	PPh_3	213	−16.5 (t, 13)	*e*	A
$C_6H_4I_2$	$PMePh_2$	213	−17.1 (t, 15)	*e*	A
C_6H_4BrI	PPh_3	220	−16.6 and −20.0 (dt, 6, 13)	6.9, *c*	A, B
$C_6H_4Br_2$	PPh_3	220	−20.8 (t, 13.3)	7.06, *c*	B
$C_6H_4Cl_2$	PPh_3	223	−20.78 (t, 20.5)[f]	*e*	B
C_6H_5I	PPh_3	213	−20.0 (t, 14.5)	6.5 (d, 8), 7.0 (dd, 8, 8)[g]	B
		273	−20.0 (br)[h,j]	6.6 (br)[j] 7.1 (br)	
C_6H_5I	$PMePh_2$	213	−19.7 (t, 14.5)	6.7 (d, 8), 6.9 (dd, 8, 8)	B
C_6H_5I	P(*p*-tolyl)$_3$	213	−20.16 (t, 14.5)[j]	6.5 (d, 8), 7.0 (dd, 8, 8)	B
C_6H_5I	P(*p*-C_6H_4Cl)$_3$	213	−19.9 (t, 15)[j]	6.6 (d, 8), 7.0 (dd, 8, 8)	B
CH_3I	PPh_3	213	−19.6 (t, 14)	*e*	B
		293	−20.1, *b*[h]	*e*	B

[a] $[IrH_2(L')_2L_2]BF_4$, where L′ = halocarbon. [b] At which the spectrum was recorded. Exchange processes led to broadening at higher temperatures (see text). [c] In $CDCl_3$, reported as position (multiplicity, coupling constant in hertz). Abbreviations: *c* = complex, *d* = doublet, and *t* = triplet. [d] Method A or method B (see Experimental Section). [e] Ligand resonances obscured. [f] Weak resonance due to *cis*-$[IrH_2(cod)L_2]BF_4$ also seen.[5] [g] Assignments: 6.5, ortho protons; 7.0, meta protons, confirmed by decoupling experiments. [h] Broadened by exchange. [i] Some sample decompositions at 0 °C.

donors lead to a chemical shift of δ −27 to −29 and olefins to a shift of δ −10 to −14. The values for $C_6H_4I_2$ (δ −16.5) and C_6H_4BrI (δ −16.6 and −20.0) suggest that H trans to halogen occurs in the range δ 16–21.

Hydrogenation of 3 in the presence of *o*-dichlorobenzene gives a solution, which at 233 K shows a sharp triplet resonance at δ −20.8 ($^2J_{PH}$ = 20.6 Hz). The addition of EtOH leads to this peak being replaced by that due to $[IrH_2(EtOH)_2L_2]^+$. Although no $C_6H_4Cl_2$ complex could be isolated, we believe $[IrH_2(C_6H_4Cl_2)L_2]^+$ may be formed in situ. When the temperature is raised to 293 K, the peak at δ −20.8 in the spectrum of the hydrogenation product collapses probably due to a process similar to that discussed above for the C_6H_4IBr case.

Reactions between both *cis*- and *trans*-ClCH=CHCl and 1 were observed by ^{1}H NMR spectroscopy, but no conclusions could be drawn as to the nature of the products, which could not be isolated.

We wished to see whether chelation was necessary for complexation. Iodobenzene did not react with 1 at 0 °C to give an isolable product, but hydrogenation of 3 in $CDCl_3$ containing C_6H_5I at 0 °C gave a solution, which on cooling to 213 K showed a triplet resonance at δ −20.0 ($^2J_{PH}$ = 14.6 Hz) which can probably be ascribed to $[IrH_2(C_6H_5I)_2L_2]^+$. A similar fluxional process to that mentioned above is probably responsible for the broadening of the Ir–H resonance when the solution is warmed. After some hours at room temperature, decomposition was evident from irreversible changes in the NMR spectrum, and all efforts to obtain a crystalline product failed.

The $PMePh_2$ analogue was prepared similarly by hydrogenation of 3 (L = $PMePh_2$), but some *cis*-$[IrH_2(cod)(PMePh_2)_2]$ was observed at 213 K as well as the presumed $[IrH_2(C_6H_5I)_2L_2]^+$. Analogous compounds were also obtained from tri-*p*-tolylphosphine and tris(*p*-chlorophenyl)phosphine.

In each case involving C_6H_5I peaks of equal intensity assigned to coordinated aryl halide were observed at δ 6.5–6.7 and 6.7–7.0. Decoupling experiments suggested these were the ortho and meta protons, respectively. These peaks broaden and shift downfield when the solution is warmed to room temperature. The addition of EtOH (10 molar equiv) to a solution of $[IrH_2(C_6H_5I)_2(PPh_3)_2]^+$ led to the immediate disappearance of the peaks we assign to coordinated C_6H_5I and the replacement of the Ir–H peak at δ −20 with a similar triplet at δ −29.4 due[7] to $[IrH_2(EtOH)_2L_2]^+$. This helps to confirm our assignment and shows that iodobenzene is even more weakly bound than C_6H_4BrI.

In no case was binding via the aromatic ring (e.g., η^6-$C_6H_4X_2$) observed, in spite of the fact that arene derivatives such as $[(\eta^6\text{-PhEt})IrL_2]BF_4$[9] can be formed from 1.

1 reacts with MeI to give $[IrH_2(MeI)_2L_2]^+$, and the same complex can also be obtained by hydrogenation of 3 in CH_2Cl_2 containing MeI. The Ir–H absorption at δ −19.76 in the ^{1}H NMR at 213 K appears as a triplet ($^2J_{PH}$ = 14 Hz) and coordinated MeI appears as a broad singlet at δ 1.2.

This complex is thermally stable and survives heating to room temperature. The MeI complex can be isolated in low yield as colorless crystals. Displacement of the MeI with MeCN in an NMR experiment gives free MeI and the known $[IrH_2(MeCN)_2L_2]^+$. EtOH gives incomplete displacement, in contrast to the complete displacement found in the C_6H_5I complex, suggesting that MeI is slightly more strongly bound, perhaps for steric reasons.

EtI and *i*-PrI give analogous complexes, as judged by the very similar ^{1}H NMR spectra obtained although these cannot be isolated as crystalline materials.

We have not been able to make Ir(I) analogues of these species, for example, by treating $[IrCl(cod)]_2$ with Ag^+ or Et_3O^+ in the presence of $C_6H_4I_2$ or MeI or by the attempted dehydrogenation of 2 with olefins.

Other materials were also examined but without complex formation being apparent: *o*-bromochlorobenzene, *o*-nitroiodobenzene, *cis*-2,3-dibromobutene, *o*-dibromomethylxylene, and xenon.

Catalytic Studies. Even though potential ligands such as PhCl do not form isolable complexes under conditions we have examined, evidence for binding has been obtained from catalytic studies.[7] In the hydrogenation of cyclohexene by $[Ir(cod)(PMePh_2)_2]BF_4$ (pH_2, 62 cmHg, 0 °C, solvent CH_2Cl_2, substrate 0.5 M, catalyst 0.5 mM), the presence of 1 molar equiv of PhCl/mol of Ir is sufficient to reduce the reaction rate to 58% of its value in pure CH_2Cl_2. For comparison, *i*-PrOH and C_6H_5I are equally strong inhibitors (rate 58–60%). These effects are far too large to be classical solvent effects but imply bonding.

$C_6H_4I_2$ completely inhibits hydrogenation (rate 0%), and $C_6H_4Br_2$ is only a weak inhibitor (rate 85%).

Conclusion

We have prepared the first series of halocarbon complexes and crystalographically characterized one example. The Ir–I bond lengths are normal, but the ligands are bound relatively weakly and they can all be displaced by MeCN, for example. The displacement experiments suggest that the formation constants decrease in the approximate order $C_6H_4I_2 > C_6H_4BrI > RI$ (R = Me, Et, *i*-Pr) $> C_6H_5I > C_6H_4Br_2 > C_6H_4Cl_2$. In contrast to groups 5 and 6 where binding of soft metals tends to be strongest with the second-row element (PR_3 or SR_2), in group 7 the strongest binding occurs with RI. The same trend has been noted for the group 7 anions, X^-.[15] In the earlier members of the series, RCl and RBr, the halogen is probably too electronegative to act as a substantial σ donor unless it bears a full negative charge, as in X^-.

These complexes provide models for probable intermediates in oxidative addition of RX. In spite of controversy about the details of mechanism,[16] many RX additions are thought to go *via* radical pathways. Electron transfer can reasonably be envisaged as taking place within an RX complex (eq 1), for which 2 provides the first crystallographically characterized model.

$$M \xrightarrow{RX} RX \rightarrow M \xrightarrow{e^- \text{ transfer}} X\text{–}M + R\cdot \qquad (1)$$

The results also suggest that the effect of the coordinating ability of halocarbons should be taken into account when considering them as solvents for stoichiometric and catalytic reactions in organometallic chemistry.

Experimental Section

Reagents. Ammonium choroiridate was obtained from Engelhard Industries and Johnson Matthey Inc. Ligands were purchased from Aldrich Chemical Co. and distilled before use. Halocarbons were also passed through a short neutral Al_2O_3 column prior to use.

Spectroscopy. NMR spectra were recorded on a Bruker 270-MHz instrument. Chemical shifts are given in δ (ppm) relative to Me_4Si. IR spectra were recorded on a Nicolet 7000 Series FT IR in a Nujol mull.

Synthesis. Starting materials were synthesized via published procedures[6,7,17] (L = PPh_3 except where stated).

Dihydrido(1,2-diiodobenzene)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (2). $[IrH_2(Me_2CO)(PPh_3)_2]$ (40.5 mg, 0.044 mmol) was dissolved in CH_2Cl_2 (20 mL) and 1,2-diiodobenzene added (508 mg, 1.5 mmol). The addition of Et_2O led to separation of crude product, which was recrystallized from CH_2Cl_2/Et_2O: yield 41.7 mg (79%); IR ν (Ir–H) 2217 (w) cm^1. Two modifications of the product were observed: (1) an unsolvated material; (2) a 0.5 $C_6H_4I_2$ solvate. Which one is formed seems to depend on whether excess $C_6H_4I_2$ is present during crystallization or not. Anal. Calcd for $C_{42}H_{36}I_2F_4BIr$: C, 44.40; H, 3.17. Found: C, 43.77; H, 3.23. Calcd for $C_{42}H_{36}I_2F_4BIr\cdot 0.5C_6H_4I_2$: C, 41.53; H, 2.92; I, 29.30. Found: C, 41.15; H, 3.14; I, 30.46.

Displacement Reactions of 2. To samples of the complex in $CDCl_3$ in an NMR tube was added ca. 100 molar equiv of various ligands, L′. The results are given below. If no reaction took place, nr is shown, if displacement took place, dis is marked, the characteristic peaks[6,7] of $[IrH_2L'_2L_2]^+$ were observed, and if an equilibrium was established between L′ and $C_6H_4I_2$, equil is marked: THF, nr; Me_2CO, nr; EtOH, equil in favor of 2; MeCN, dis; bpy, dis.

Analogous $PMePh_2$ Complex. The $PMePh_2$ analogue was detected in a ^1H NMR experiment by the addition of $C_6H_4I_2$ (0.09 mL, 0.7 mmol) to $[IrH_2(Me_2CO)(PMePh_2)_2]BF_4$ (4 mg, 7.4 mmol) in CD_2Cl_2 at 0 °C, followed by cooling to 213 K to observed the spectrum (Table I). The tris(*p*-chlorophenyl)phosphine and tri-*p*-tolylphosphine PhI analogues were observed in a similar experiment.

Further Reactions of 2. Under the conditions described in ref 9 and 16, but substituting 2 for 1, the same products were obtained: from styrene, $[(\eta^6\text{-PhEt})IrL_2]BF_4$[9] (90%), and from cyclopentene, $[(\eta^5\text{-Cp})IrL_2H]BF_4$[6] (33%). None of this last product was obtained from cyclopentane, in contrast to the situation for 1.[6]

Collection and Reduction of X-ray Data. Crystals of $[Ir(I_2C_6H_4)[(C_6H_5)_3P]_2H_2]BF_4$ were grown from a methylene chloride/ether bilayer. All diffraction measurement were performed on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromatized Mo Kα radiation. Unit cells were determined from 25 randomly selected reflections by using the CAD-4 automatic search, center, index, and least-squares routines. The space group was determined from the systematic absences $h0l$, $l + h = 2n + 1$, and $0k0$, $k = 2n + 1$, observed during data collection.

All calculations were performed on a Digital PDP 11/45 computer using the Enraf-Nonius SDP program library. The structure was solved by the heavy-atom method. Anomalous dispersion corrections[18a] were added to the neutral-atom scattering factors[18b] used for all non-hydrogen atoms. Full-matrix least-squares refinements minimized the function $\sum\omega(F_o - F_c)^2$ where the weighting factor $\omega = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o)^2/2F_o$, and $\sigma(F_o{}^2) = [\sigma(I_{raw})^2 + (pF_o{}^2)^2]^{1/2}/Lp$. Crystallographic data for the structure is listed in Table I.

A crystal of dimensions 0.348 mm × 0.175 mm × 0.073 mm was selected and mounted in a thin-walled glass capillary. The major crystal faces were identified as $\bar{1}21$, $12\bar{1}$, $1\bar{2}\bar{1}$, $\bar{1}\bar{2}1$, $\bar{1}0\bar{2}$, and 102. ω scan peak widths at half-peak height were in the range 0.1–0.2°. The crystal was mounted with the normal to the 102 plane oriented 2.09° from the difractometer ϕ axis. From a total of 5461 reflections, 3026 ($F^2 \geq 3.0\sigma(F^2)$) were used in the structure solution and refinement. Standard reflections monitored periodically showed only a random (±2%) fluctuation during data collection. After correction for absorption, full-matrix least-squares refinement using anisotropic thermal parameters for the iridium, phosphorus, iodine, and fluorine atoms and isotropic thermal parameters for the remaining non-hydrogen atoms converged to the final residuals $R_1 = 0.047$ and $R_2 = 0.050$. Hydrogen atoms were not included in the calculation. The largest peaks in the final difference Fourier synthesis were 0.56–0.96 $e^-/Å^3$ and were clustered about the metal atom. The largest value of the shift/error parameter on the final cycle of refinement was 0.18. The error in an observation of unit weight was 1.78. Final atomic coordinates and thermal parameters are listed in Table II. Bond distances and angles with errors from the inverse matrix obtained on the final cycle of least-squares refinement are listed in Tables III and IV.

Complexes with Other Halocarbons. 1,2-Bromoiodobenzene. Method A. C_6H_4BrI (0.2 mL, 1.6 mmol) was added to $[IrH_2(Me_2CO)L_2]BF_4$ (50 mg, 0.054 mmol) in CH_2Cl_2, and the colorless product isolated with Et_2O, and recrystallized from CH_2Cl_2/Et_2O; yield 15 mg (25%). Satisfactory analyses were never obtained.

Method B. The complex could also be detected in a ^1H NMR experiment in which $[Ir(cod)L_2]BF_4$ (4 mg, 7.4 mmol) was dissolved in $CDCl_3$ (0.5 mL) in an NMR tube and the ligand added (0.23 mL, 1.8 mmol). H_2 (30 mL/min) was bubbled through the solution at 0 °C for 10 min. The resulting spectrum, recorded at 213 K (Table V), was identical with that for the complex isolated by method A, except that a singlet at δ 1.46 assigned to cyclooctane was also seen. Displacement studies: EtOH, dis; MeCN, dis; bpy, dis.

1,2-Dibromobenzene. Material isolated by method A gave a ^1H NMR spectrum that was not consistent with the formation

---

[15] Ahrland; Chatt, J.; Davies *Q. Rev., Chem. Soc.* **1958**, *12*, 265.

[16] Lappert, M. F.; Lednor, P. W. *Adv. Organomet. Chem.* **1976**, *14*, 345.

[17] Crabtree, R. H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *135*, 395.

[18] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol IV: (a) Table 2.3.1., pp 149–50; (b) Table 2.2B pp 99–101.

of a complex of type 2 (δ 4.7, 3.5 and 2.9 (s); −18.6 and −23.0 (dt, 8, 16); −29.2 (t, 16)). The complex was observed by method B and was isolated with Et_2O as an unstable colorless solid.

Iodobenzene. Method A gave no isolable products. Method B gave the spectra shown in Table I, which we assign to $[IrH_2(C_6H_5I)_2L_2]BF_4$. Displacement study (L = PPh_3): EtOH, dis.

Iodomethane. $[IrH_2(MeI)_2(PPh_3)_2]BF_4$ could be made by method A from the acetone complex (50 mg, 0.054 mmol) and MeI (0.2 mL, 2.2 mmol) in CH_2Cl_2 (20ml) and was isolated with Et_2O; yield 22 mg, 0.2 mmol (40%). Method B gave the same complex which was formed in essentially quantitative yield but could only be isolated in poor yield (~20%) as colorless crystals with Et_2O (ν(IrH) 2210 (w) cm^{-1}). Displacement studies: EtOH, equil in favor of 1; MeCN, dis. EtI and *i*-PrI gave analogous complexes by method B, but these were not isolated. CH_2I_2 did not give identifiable materials by either method. Satisfactory analyses were never obtained, probably due to the thermal instability of the complexes at 20 °C over several days, except for the MeI complex. Anal. Calcd for $C_{38}H_{38}I_2F_4BIr$: C, 41.87; H, 3.49. Found: C, 41.96; H, 3.66.

Catalytic Studies. The method described in ref 7 was used to measure the effect of the halocarbons (1 molar equiv/mol of Ir) on cyclohexene hydrogenation by $[Ir(cod)(PMePh_2)_2]PF_6$. Rates observed relative to CH_2Cl_2 (100%) were as follows: $C_6H_4I_2$, 0%; $C_6H_5Br_2$, 78%; $C_6H_5Cl_2$, 105%; C_6H_5I, 60%; C_6H_5Br, 110%, C_6H_5Cl, 60%.

Acknowledgment. We thank National Science Foundation and the Petroleum Research Fund for support, Professor Richard Adams for helpful discussions, Doug Anton for IR data and the A.P. Sloan and Camille and Henry Dreyfus Foundations for Fellowships (to R.H.C.).

Registry No. *cis,trans*-$[IrH_2(o\text{-}C_6H_4I_2)(PPh_3)_2]BF_4$, 82582-50-1; *cis,trans*-$[IrH_2(o\text{-}C_6H_4I_2)(PPh_2Me)_2]BF_4$, 82598-64-9; *cis,trans*-$[IrH_2(o\text{-}C_6H_4IBr)(PPh_3)_2]BF_4$, 82582-52-3; *cis,trans*-$[IrH_2(o\text{-}C_6H_4Br_2)(PPh_3)_2]BF_4$, 82582-54-5; *cis,trans*-$[IrH_2(o\text{-}C_6H_4Cl_2)(Ph_3)_2]BF_4$, 82582-56-7; $[IrH_2(IPh)_2(PPh_3)_2]BF_4$, 82582-58-9; $[IrH_2(IPh)_2(PPh_2Me)_2]BF_4$, 82582-60-3; $[IrH_2(IPh)_2(C_6H_4Me\text{-}p)_2]BF_4$, 82582-62-5; $[IrH_2(IPh)_2(C_6H_4Cl\text{-}p)_2]BF_4$, 82582-64-7; $[IrH_2(IMe)_2(PPh_3)_2]BF_4$, 82582-66-9; *cis,cis,trans*-$[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$, 82582-67-0.

Supplementary Material Available: A listing of observed and calculated structure factors and tables further bond lengths and angles and molecular planes (13 pages). Ordering information is given on any current masthead page.

Regio- and Stereospecific Nucleophilic Additions to a Metal-Substituted Carbonium Ion, $[PtI\{MeC_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]BF_4$. A Unique Reversible Aryl to Cyclohexadiene Conversion at a Platinum(II) Center

David M. Grove, Gerard van Koten,* and Henk J. C. Ubbels

Anorganisch Chemisch Laboratorium, J.H. van't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, 1018WV Amsterdam, The Netherlands

Received April 21, 1982

The cationic complex $[PtI\{MeC_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]BF_4$, 1, which can be described as a metal-substituted arenonium ion, is susceptible to attack by anionic nucleophilic reagents. At room temperature or above aqueous reagents give rise to products resulting from cleavage of either the single C–Me or C–Pt σ bond. At lower temperature in appropriate solvents bases such as $PhC{\equiv}C^-$, $CH(CO_2Me)_2^-$, OMe^-, and OH^- produce neutral products arising from nucleophilic addition to the substituted C_6H_3 ring. Two types of product are possible with a metal-substituted cyclohexa-2,4-diene or cyclohexa-2,5-diene ring system, corresponding respectively to either "ortho" or "para" addition to the arenonium ion. Of these neutral species only the phenylacetylide complex does not react with anhydrous HBF_4 to regenerate 1. Together with the formation of 1 from the interaction of $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}(H_2O)]BF_4$, 2, with MeI the reactions reported form a unique, fully reversible, aryl-to-cyclohexadiene conversion in a metal coordination sphere.

Introduction

One of the most fundamental areas in organometallic chemistry is the study of the activation of organic molecules by metal centers. Surveys of the coordination chemistry of nickel,[1] palladium,[2,3] and platinum[3,4] have been made, and there is current interest in complexes of these metals containing delocalized systems such as allyl,[5] arene,[6] and cyclopentadienyl.[7-9] During studies of a platinum system containing a σ-bonded aryl ring with "built-in" ligand substituents, i.e., $[PtBr\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$, which has trans-situated N donor atoms, we isolated an unusual complex, $[PtI\{MeC_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]BF_4$, 1,[10,11] the structure of which (determined by X-ray methods) is shown in Figure 1. This information together with ^1H NMR data and CNDO/S calculations suggests that the C_6 ring is σ bonded to the square-planar platinum(II) center and as a consequence the positive charge of this cation is to a large degree located within the clearly nonplanar ring. This description infers

---

(1) Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1974; Vol. 1.

(2) Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol. 1.

(3) Hartley, F. R. "The Chemistry of Platinum and Palladium"; Applied Science Publishers: London, 1973.

(4) Belluco, U. "Organometallic and Coordination Chemistry of Platinum"; Academic Press: London, 1974.

(5) Henc, B.; Jolly, P. W.; Salz, R.; Stobbe, S.; Wilke, G.; Mynott, R.; Seevogel, K.; Goddard, R.; Kruger, C. J. *J. Organomet. Chem.* **1980**, *191*, 449–475.

(6) Gastinger, R. G.; Klabunde, K. J. *Transition Met. Chem. (Weinheim, Ger.)* **1979**, *4*, 1–13.

(7) Goel, A. B.; Goel, S.; van der Weer, D.; Clark, H. C. *Inorg. Chim. Acta Lett.* **1981**, L113.

(8) Werner, H., Kühn, A.; Burschka, C. *Chem. Ber.* **1981**, *113*, 2291–2307.

(9) Werner, H.; Dernberg, T. *J. Organomet. Chem.* **1980**, *198*, 97–103.

(10) van Koten, G.; Timmer, K.; Noltes, J. G.; Spek, A. L. *J. Chem. Soc. Chem. Commun.* **1978**, 250–252.

(11) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.*, in press.

0276-7333/82/2301-1366$01.25/0