Table I. Binding Energies (eV) of Some Iridium Complexes (±0.3 eV)

substrate	$Ir(4f_{5/2})$	$Ir(4f_{7/2})$	reaction 2	$Ir(4f_{5/2})$	$Ir(4f_{7/2})$	reaction 1	$Ir(4f_{5/2})$	$Ir(4f_{7/2})$
[Ir(phen)(cod)]Cl	66.3	62.7	$[Ir(phen)(cod)PPh_3]Cl$	65.8	62.3	$[Ir(phen)(cod)Cl_2]PF_6$	68.2	64.8
			[Ir(phen)(cod)SCN]	65.6	62.3	$[Ir(phen)(cod)HCl]PF_6$	68.2	64.7
			[Ir(phen)(cod)I]	65.7	62.4	$[Ir(phen)(cod)CH_3I]I$	67.8	64.2
			$[Ir(phen)(cod)(C_2H_2)]Cl$	66.3	62.8	$[Ir(phen)(cod)O_2]I$	66.8	63.5
			$[Ir(phen)(cod)(C_2H_4)]Cl$	66.4	63.0			
$[Ir(dppe)_2]Cl$	67.0	63.5	$[Ir(dppe)_2CO]Cl$	66.6	63.1	$[Ir(dppe)_2O_2]Cl$	67.3	63.9
$[IrCl(CO)(PPh_3)_2]$	66.2	62.6				$[IrCl(CO)(PPh_3)_2O_2]$	67.4	64.0
$[IrCl(PPh_3)_3]$	65.8	62.5				$[IrCl(PPh_3)_3O_2]$	66.7	63.3

Table II. Relative Oxidation Number (ON) of Products of Iridium(I) Complex Reactions with Various Small Molecules

substrate	L or XY	ON	ON[a]
[Ir(phen)(cod)]Cl	SCN^-	0.26	
	I^-	0.37	
	PPh_3	0.47	
	C_2H_2	1.00	
	C_2H_4	1.11	
	O_2	1.53	1.89
	CH_3I	2.58	2.48
	HCl	3.00	2.46
	Cl_2	3.00	3.00
$[Ir(dppe)_2]Cl$[b]	CO	0.6	
	O_2	1.3	
$[IrCl(PPh_3)_3]$[b]	O_2	1.9	
$[IrCl(CO)(PPh_3)_2]$[b]	O_2	2.2	1.89

[a] Values obtained by Vaska on the basis of ν_{CO} stretching frequencies for the complex $[IrCl(CO)(PPh_3)_2]$. [b] Values based on the assumption that the Ir(4f) binding energies of the Cl_2 adducts of these complexes will increase by 1.9 eV.

Studies on [Ir(cod)(phen)L]Cl Where L = SCN^-, I^-, PPh_3, C_2H_2, or C_2H_4

The reactions of these L molecules are generally accepted to be simply addition reactions. In contrast to ligands such as $C_2(CN)_4$, $C_2(Ph)_2$, and C_2F_4 where considerable metal-to-ligand charge transfer has been noted[6,10] C_2H_2 and C_2H_4 show no net charge transfer in [Ir(phen)(cod)L]Cl (Table II). This can be explained by similar σ-bonding and π-back-bonding effects. However, in the softer $[Pt(PPh_3)_2(C_2H_4)]$ complex the oxidation number of platinum was estimated[19] to be +0.8, indicating that this complex has a much greater π-back-bonding component.

As expected, a considerable ligand-to-metal charge transfer is obtained for L = SCN^-, I^-, PPh_3, and CO. Kinetically PPh_3 and CO are better nucleophiles[16] than SCN^- and I^-, but their ability to participate in π back-bonding is most probably the reason why iridium oxidation numbers of 0.47 and 0.6 are obtained for PPh_3 and CO as compared to the 0.26 and 0.37 values for SCN^- and I^-, respectively.

Studies on Dioxygen Uptake

There has been much speculation as to whether this reaction should be considered an addition or oxidative-addition reaction.[9] From Table II it is clear that some charge has been accepted by the dioxygen molecule for all the complexes studied.

The kinetics and mechanism of the reaction Ir(phen)(cod)X + O_2 → $[Ir(phen)(cod)O_2]^+$ + X^- where X = Cl, I, or SCN have been published recently.[17] For X = Cl the starting complex is four-coordinate (Cl being the counterion) while I^- and SCN^- bind reversibly to form five-coordinate complexes.[10a] It was found that the rate of oxygen uptake increases in the series $Cl^- \ll I^- < SCN^-$. As is shown in Table II, SCN^- and I^- donate electrons into the iridium center, making it a much better nucleophile, and therefore enhancing the rates of oxidative additions toward electrophiles.[17-19] This is therefore in keeping with dioxygen adding oxidatively to metal complexes.

The data presented here and elsewhere[20] clearly show that a distinction between oxidation states is often very difficult to make since a range of binding energies can be found within a formal oxidative state.

Registry No. [Ir(phen)(cod)]Cl, 53522-11-5; $[Ir(dppe)_2]Cl$, 15390-38-2; $IrCl(CO)(PPh_3)_2$, 14871-41-1; $IrCl(PPh_3)_3$, 16070-58-9; $[Ir(phen)(cod)PPh_3]Cl$, 80263-33-8; Ir(phen)(cod)SCN, 66779-01-9; Ir(phen)(cod)I, 41392-85-2; $[Ir(phen)(cod)(C_2H_2)]Cl$, 80263-34-9; $[Ir(phen)(cod)(C_2H_4)]Cl$, 80263-35-0; $[Ir(dppe)_2CO]Cl$, 15308-58-4; $[Ir(phen)(cod)Cl_2]PF_6$, 80263-37-2; $[Ir(phen)(cod)HCl]PF_6$, 53522-18-2; $[Ir(phen)(cod)CH_3I]I$, 80287-61-2; $[Ir(phen)(cod)O_2]I$, 80263-38-3; $[Ir(dppe)_2O_2]Cl$, 19214-64-3; $IrCl(CO)(PPh_3)_2O_2$, 15187-10-7; $IrCl(PPh_3)_3O_2$, 42583-98-2.

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Enthalpy of the Oxidative Addition of Tetrachloro-1,2-benzoquinone to $\{M[cis\text{-}(C_6H_5)_2PCHCHP(C_6H_5)_2]_2\}BF_4$ (M = Cobalt, Rhodium, or Iridium)

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We wish to report a study of the enthalpy change for oxidative-addition reactions at square-planar cobalt(I), rhodium(I), and iridium(I) centers. Direct comparison of the three metals in this way is rarely possible due to differing structural requirements. the oxidative-addition reaction is found as a step in numerous catalytic and stoichiometric reactions of four-coordinate, d^8 complexes.[1-3] This has been studied in some detail for rhodium(I) and iridium(I) since numerous four-coordinate complexes have been synthesized and conveniently handled.[4,5] For cobalt(I), a coordination number of five is most favorable and oxidative addition requires prior dissociation of one ligand.[4] Hence direct comparison of reactivity of the three metals is not usually possible.

The synthesis of $CoCl(PPh_3)_3$ has been reported,[6] but this complex is presumed to be tetrahedral and lacks the reactivity of square-planar cobalt(I) or of analogous rhodium(I) and

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iridium(I). Chen[7] used the triphenylphosphine complex as a starting material to obtain a set of cationic complexes believed to be of the type $[Co(P{-}P)_2]X$, where P–P is a bidentate tertiary phosphine and X is Cl, BPh_4, or PF_6. These were in general unstable and poorly characterized due to their sensitivity to air. The best characterized complex was obtained with the ligand *cis*-1,2-bis(diphenylphosphino)ethylene, $Ph_2PCH{=}CHPPh_2$. It forms a stable dioxygen complex[7,8] analogous to known cationic rhodium and iridium[9] dioxygen complexes. In this case also the cobalt(I) compound was found to decompose on standing within days.[7]

The existence of $[M(cis\text{-}Ph_2PCH{=}CHPPh_2)_2]^+$ for all three metals suggested the chance for a comparison of heats of oxidative addition reactions, which are now reported.

Experimental Section

The complexes *trans*-$[IrCl(N_2)(PPh_3)_2]$[10] and $[RhCl(1,5\text{-}C_8H_{12})]_2$[11] were prepared by methods in the literature. The complexes $[M(Ph_2PCH{=}CHPPh_2)_2]BF_4$ (M = Rh, Ir) were prepared by methods other than those reported in the literature,[7,12] and for M = Co, a modification of the method of Chen[7] was used. The air-sensitive M(I) complexes and their solutions were carefully handled in a nitrogen atmosphere. Nitrogen-purged solvents were used on all occasions. $O_2C_6Cl_4$ (Aldrich) was used as received, and 1,2-dichloroethane was distilled from P_4O_{10} before use. IR spectra were recorded on a Perkin-Elmer Model 621 spectrometer. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Electronic spectra were recorded on a Cary 214 spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

$[Co(Ph_2PHC{=}CHPPh_2)_2]BF_4$. $CoCl(PPh_3)_3$, 2.70 g (3.07 mmol), and *cis*-$Ph_2PHC{=}CHPPh_2$, 2.80 g (7.07 mmol), were placed in a two-flask Schlenk filtration setup under N_2. Ethanol, 70 mL, was injected into the reaction flask with stirring. This mixture was heated with a heat gun until the solution turned dark green (2–3 min). The solution was cooled to room temperature and filtered by inverting the apparatus. A 0.5 M $LiBF_4$–ethanol solution, 9 mL, which had been previously filtered, was slowly injected into the dark green solution. This solution was stirred for 20 min, placed in an ice bath for 1 h, and then filtered. The dark green crystals were washed twice with 3-mL portions of ether: yield 2.34 g (81.3%); mp 300–302 °C. To recrystallize this, we dissolved 0.62 g of the product in 10 mL of CH_2Cl_2 in a two-flask filtration apparatus. This solution was filtered under N_2. CH_3OH (10 mL) was injected into the filtered solution, and a slow stream of N_2 was used to evaporate the CH_2Cl_2 and precipitate the dark green crystals. The product was washed three times with 2-mL portions of ether. A yield of 0.18 g was recovered; mp 314–316 °C. Anal. Calcd for $C_{52}H_{44}BF_4P_4Co$: C, 66.55; H, 4.73. Found: C, 66.71; H, 4.94.

$[Co(O_2C_6Cl_4)(Ph_2PCH{=}CHPPh_2)_2]BF_4$. $[Co(Ph_2PHC{=}CHPPh_2)_2]BF_4$, 0.11 g (0.12 mmol), was dissolved in 10 mL of CH_2Cl_2 under N_2. A 0.054 M solution of $C_6Cl_4({=}O)_2$ in CH_2Cl_2, 6 mL, was injected into the reaction flask. The green crystals were precipitated with ether: yield 0.09 g (63.4%); mp 214 °C. The product was recrystallized twice from methylene chloride with ether; mp 214–216 °C. Anal. Calcd for $C_{58}H_{44}Cl_4O_2P_4BF_4Co$: C, 58.82; H, 3.74; Cl, 11.97. Found: C, 58.83; H, 4.15; Cl, 10.77.

$[Rh(Ph_2PCH{=}CHPPh_2)_2]BF_4$. $[RhCl(COD)]_2$, 0.25 g (0.5 mmol) (COD = 1,5-cyclooctadiene), and *cis*-$Ph_2PCH{=}CHPPh_2$, 0.80 g (2.0 mmol), were stirred in 20 mL of benzene under nitrogen for 2 h to have $[Rh(Ph_2PCH{=}CHPPh_2)_2]Cl$. It was dissolved in 15 mL of methanol and filtered into another flask under a current of nitrogen. $NaBF_4$, 0.05 g (0.46 mmol), in water was added, and the yellow $[Rh(Ph_2PCH{=}CHPPh_2)_2]BF_4$ (mp 285–290 °C dec) was recovered by filtration from the cold solution. It was then washed with cold methanol containing $NaBF_4$, water, and diethyl ether; yield 0.90 g (90%). Anal. Calcd for $C_{52}H_{44}BF_4P_4Rh$: C, 63.57; H, 4.51. Found: C 63.62; H, 5.05.

$[Ir(Ph_2PCH{=}CHPPh_2)_2]BF_4$. $IrClN_2(PPh_3)_2$, 0.50 g (0.64 mmol), and *cis*-$Ph_2PCH{=}CHPPh_2$, 0.56 g (1.40 mmol), were stirred under nitrogen in 15 mL of benzene for 3 h. $[Ir(Ph_2PCH{=}CHPPh_2)_2]Cl$ was filtered and washed with benzene and diethyl ether. It was then dissolved in 10 mL of methanol and filtered, and addition of $NaBF_4$ as before yielded 0.63 g (91.8%) of orange $[Ir(Ph_2PCH{=}CHPPh_2)_2]BF_4$ (mp 270–275 °C dec). Anal. Calcd for $C_{53}H_{48}BF_4P_4OIr$ (includes 1.0 mol of CH_3OH): C, 57.67, H, 4.38. Found: C, 56.94; H, 4.47.

$[Rh(O_2C_6Cl_4)(Ph_2PCH{=}CHPPh_2)_2]BF_4$. $[Rh(Ph_2PCH{=}CHPPh_2)_2]BF_4$, 0.072 g (0.073 mmol), and $O_2C_6Cl_4$, 0.019 g (0.077 mmol), were dissolved under nitrogen in 1,2-dichloroethane. Addition of 4 mL of diethyl ether yielded 0.08 g (89%) of the purple complex. Anal. Calcd for $RhC_{59}H_{46}BF_4P_4Cl_5O_2$ (as the hemisolvate of $C_2H_4Cl_2$): C, 55.45; H, 3.63; Cl, 13.87. Found: C, 55.23; H, 3.66; Cl, 13.80.

$[Ir(O_2C_6Cl_4)(Ph_2PCH{=}CHPPh_2)_2]BF_4$. With use of the method for the rhodium analogue, $[Ir(Ph_2PCH{=}CHPPh_2)_2BF_4$, 0.11 g (0.10 mmol), and $O_2C_6Cl_4$, 0.03 g (0.12 mmol), gave 0.13 g (96.3%) of the deep orange complex. Anal. Calcd for $IrC_{59}H_{46}BF_4P_4Cl_5O_2$ (as the hemisolvate of $C_2H_4Cl_2$): C, 51.83; H, 3.39; Cl, 12.97. Found: C, 51.47; H 3.39; Cl, 13.23.

Calorimetry. A Tronac 450-4 titration calorimeter was used. In general 0.07–0.10 g of the metal complx was placed in a 2-mL volumetric flask and the flask was purged with N_2 for 25–30 min. 1,2-Dichloroethane purged with N_2 was added to the mark, and the solution was transferred to the titration buret under a slow stream of N_2. A 0.07–0.12-g quantity of tetrachloro-*o*-benzoquinone was placed in the reaction vessel, which was purged with argon for 25–30 min. 1,2-Dichloroethane, 40 mL, was added to the reaction vessel via syringe through a Teflon delivery tube. A series of aliquots of the metal complex solution were added via buret to the tetrachloro-*o*-benzoquinone solution, and the heat change for each addition was evaluated. The reaction is found to be slow as the titration approaches the end point, and consequently error in ΔH becomes high. So the metal complex solution was titrated into a tenfold excess of tetrachloro-*o*-benzoquinone solution. Titrations for the cobalt complex were carried out in a reverse way due to its high sensitivity toward air. The stoichiometry of reaction was established by titrating an excess of $O_2C_6Cl_4$ into the metal complex solution in the reaction vessel. The end points were reached with a $O_2C_6Cl_4$:complex mole ratio of 1.0 ± 0.1. All the reactions studied were quantitative presumably with $K > 10^5$. ΔH values were obtained directly from the experimental heat values. No heat change due to dilution was observed when solutions of the metal complexes or $O_2C_6Cl_4$ were titrated with the solvent 1,2-dichloroethane. The standard resistance heater was calibrated periodically by HCl–tris(hydroxymethyl)aminomethane titration. The observed $\Delta H = -47.49 \pm 0.96$ kJ/mol is consistent with the literature value of −47.49 kJ/mol.[13]

Results and Discussion

We have found the tetrafluoroborate salts of the cations $M[Ph_2PCHCHPPh_2]_2^+$ (M = Co, Rh, or Ir) to be convenient to handle and store. Even the cobalt complex, which has been reported to be unstable as PF_6^- or BPh_4^- salts, can be stored indefinitely at room temperature in sealed ampules as the BF_4^- salt. Synthesis of the chloride salt of the iridium complex from the dinitrogen complex, reaction 1, has the advantage of being

$$trans\text{-}[IrCl(N_2)(PPh_3)_2] + P{-}P \xrightarrow{C_6H_6} [Ir(P{-}P)_2]Cl + 2PPh_3 + N_2 \quad (1)$$

$$P{-}P = cis\text{-}Ph_2PCHCHPPh_2$$

quantitative at room temperature within a few minutes. This is in contrast to the usual method beginning with *trans*-$[IrCl(CO)(PPh_3)_2]$, which requires prolonged reflux at high

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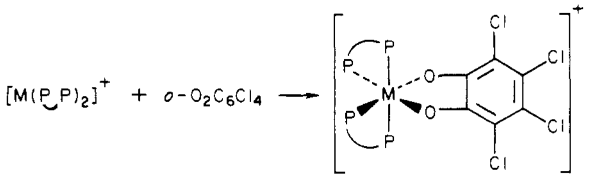
Table I. Enthalpy Data for the Reaction between $[M(Ph_2PCH{=}CHPPh_2)_2]BF_4$ and $O_2C_6Cl_4$ in 1,2-Dichloroethane at 25 °C

M	$-\Delta H$,[a] kJ/mol
Co	196 ± 11
Rh	144 ± 9
Ir	179 ± 8

[a] Error limits are 1 standard deviation of the mean of at least 12 determinations.

temperatures in order to eliminate carbon monoxide from the initial reaction product, which is $[Ir(CO)(Ph_2PCHCHPPh_2)_2]^+$.[9] The analogous rhodium complex is readily obtained from $[RhCl(1,5\text{-}C_8H_{12})]_2$ in a similar way.

When a solution of $[M(Ph_2PCH{=}CHPPh_2)_2]BF_4$ was tritrated with a solution of tetrachloro-*o*-benzoquinone, heat was liberated and the end point reached with equimolar amounts of the reactants. Further addition of the titrant produced no heat change, showing 1:1 stoichiometry. A similar result was obtained in the reverse titration. The stoichiometry was further confirmed by isolation of $[M(O_2C_6Cl_4)(Ph_2PCH{=}CHPPh_2)_2]BP_4$ from solutions of rather higher concentrations than those used in calorimetric titrations. The reaction shown in eq 2 is clean and quantitative.



(2)

M = Co, Rh, or Ir

The tendency of d^8 complexes to undergo oxidative addition increases in going from the second to the third transition series in a given group of the periodic table.[4] The relative position of the metal in the first transition series is often not known because the appropriate complexes are not available. Quantitative comparison of their reactivity toward various addends is only possible with complexes having a similar ligand environment.[3,5]

The complexes $[M(Ph_2PCH{=}CHPPh_2)_2]^+$ have a planar structure[14] like $[M(Ph_2PCH_2CH_2PPh_2)_2]^+$[15] and many other d^8 complexes. The higher reactivity of the iridium complex over the rhodium analogue is suggested by the fact that $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$ readily adds hydrogen to give six-coordinate Ir(III) but the corresponding Rh complex does not.[14,16] The crystal structure of the dioxygen adducts $[M(O_2)(Ph_2PCH_2CH_2PPh_2)_2]PF_6$[17] (M = Rh, Ir) shows that the Ir–O bonds are longer compared to the Rh–O bonds. Vaska has suggested on the basis of qualitative evidence that the stability of adducts is Co > Ir > Rh.[9]

Table I shows the enthalpy data obtained from calorimetric titrations. Comparison of data shows that $\Delta H_{\mathrm{Rh}} \approx 0.8(\Delta H_{\mathrm{Ir}})$, which agrees well with the ΔH ratio for the reaction of $MX(CO)L_2$ (M = Rh, Ir) with $O_2C_6Cl_4$ in benzene.[18] It is also observed qualitatively here that the sequence of reactivity (kinetic) of the three metal complexes for oxidative addition is Co > Ir > Rh. Since the reactions are virtually quantitative having $K \gtrsim 10^5$ L/mol, it is not possible to compare quantitatively the adduct stabilities, which are very likely to be consistent with the order suggested by Vaska[9] for formation of $[M(O_2)(Ph_2PCH{=}CHPPh_2)_2]^+$ in chlorobenzene. The enthalpy data when compared to data[17] for $MX(CO)(PPh_3)_2$ indicate that the chelate complexes form stronger bonds with $O_2C_6Cl_4$ and may thus by considered as stronger bases. This coincides with the fact that H_2 and O_2 addition to $[Ir(Ph_2PCH_2CH_2PPh_2)_2]^+$ is irreversible while these molecules are readily removed from *trans*-$[IrCl(CO)(PPh_3)_2]$ by heating.[9] The higher enthalpy change for reaction of the cobalt complex in comparison to those of rhodium and iridium and the apparent greater reactivity toward dioxygen may arise from the relative instability of cobalt(I) in a square-planar environment.

Table II. Physical Properties of the Complexes $[M(O_2C_6Cl_4)(Ph_2PCH{=}CHPPh_2)_2]BF_4$

M	color	mp, °C	$\lambda_{\max}$, nm (ϵ)	IR for the three complexes,[a] cm^{-1}
Co	green	214–217 dec	337 (26 000)	1260 (m), ~1060 (s), 970 (m), 810 (m)
Rh	purple	365–368 dec	544 (1205)	
Ir	orange	340–342 dec	437 (1222)	

[a] Abbreviations: m, medium; s, strong.

Some of the physical properties of the oxidative-addition products are given in Table II. The complexes have high thermal stability. The intense absorption in the visible region by the cobalt complex and comparatively less intense absorptions by rhodium and iridium complexes are presumably due to charge-transfer transitions. The IR spectra of all three complexes show absorptions at the same wavelengths, indicating that the addition complexes have the same structures. Attempts to obtain satisfactory ^{1}H NMR spectra were frustrated by the low solubility of the complexes.

Acknowledgment. We gratefully acknowledge the support of the Robert A. Welch Foundation and the University of Texas at Arlington Organized Research Fund for support of this work. A loan of iridium chloride from Engelhard, Inc., is also appreciated.

Registry No. $[Co(Ph_2PHC{=}CHPPh_2)_2]BF_4$, 80243-31-8; $[Co(O_2C_6Cl_4)(Ph_2PCH{=}CHPPh_2)_2]BF_4$, 80243-33-0; $[Rh(Ph_2PCH{=}CHPPh_2)_2]BF_4$, 54293-56-0; $[Rh(O_2C_6Cl_4)(Ph_2PCH{=}CHPPh_2)_2]BF_4$, 80262-56-2; $[Ir(Ph_2PCH{=}CHPPh_2)_2]BF_4$, 80243-34-1; $[Ir(O_2C_6Cl_4)(Ph_2PCH{=}CHPPh_2)_2]BF_4$, 80243-36-3; $O_2C_6Cl_4$, 2435-53-2; $CoCl(PPh_3)_3$, 26305-75-9; $[RhCl(COD)]_2$, 12092-47-6; $IrClN_2(PPh_3)_2$, 15695-36-0.

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Synthesis and Magnetic Properties of $(Mn_{1-x}Cr_x)_3B_4$ and $(Mn_{1-x}Mo_x)_3B_4$

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Mn_3B_4 has the orthorhombic (D_{7b}) Ta_3B_4-type structure and is antiferromagnetic with a Néel temperature of 392 K. But the temperature dependence of magnetic susceptibility of Mn_3B_4 shows a second magnetic ordering at 226 K.[1] On the basis of the magnetic structure determined by neutron diffraction, Neov[2] reported that below 226 K the Mn4(g) atoms were magnetically ordered and the collinear antiferromagnetic structure was deformed to a spiral structure, and that at 4.2 K the collinear antiferromagnetic structure was recovered

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