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DESIGN OF SYSTEMS WITH EXTENDED METAL–METAL INTERACTIONS. SYNTHESES OF MONO- AND DI-NUCLEAR RHODIUM(I) AND IRIDIUM(I) COMPLEXES CONTAINING DIENES, CARBON MONOXIDE, BIPYRIDYL AND THE UREA DERIVATIVE $OC(NMePF_2)_2$

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Summary

The deep purple-red [RhCl(CO)(bipy)], black [IrCl(CO)(bipy)], and orange $[Rh(bipy)_2][BF_4]$ complexes (bipy = bipyridyl) are reported, as is the unusual hydride $[IrH(bipy)_2]CH_2Cl_2$. The newly synthesised dinuclear yellow/orange oxalato bridged compounds $[\{Rh(C_6H_{10})\}_2(C_2O_4)]$ and $[\{Ir(C_8H_{12})\}_2(C_2O_4)]$ can be converted into the purple-red $[\{Rh(CO)_2\}_2(C_2O_4)]$ and blue-black $[\{Ir(CO)_2\}_2(C_2O_4)]$ complexes, respectively.

Introduction

There is considerable current interest in new anisotropic materials having novel solid state properties [1–5]. Most studies on such "one-dimensional metal" systems involving square planar d^8 complexes have involved platinum(II), however $[IrCl(CO)_3]$ [6] displays conductivity [4–7] along the stacking axis and similarly $[Ir(acac)(CO)_2]$ [8] is an intrinsic semiconductor. Several rhodium(I) complexes also form linear stacks e.g. $[Rh(acac)(CO)_2]$ [9] and [RhCl(CO)pzH] (pzH; pyrazole) [10].

We recently reported the single crystal structure of $[IrCl(PF_3)_2]_2$ which has an unusual zig-zag chain structure similar to that in $[RhCl(CO)_2]_2$ but with much stronger bonding [11,12], and we have described the factors that are important in determining whether extended metal–metal interaction will occur [12]. Of particular interest is the use of sterically undemanding and/or planar ligands, and in this paper we report our results of a study of several diene and carbonyl complexes of rhodium(I) and iridium(I) and their interaction with the planar ligands bipyridyl, $OC(NMePF_2)_2$ and oxalate ion.

Results and discussion

Lawson and Wilkinson were unable to isolate pure [RhCl(CO)(bipy)] (I) (bipy = 2,2′-bipyridyl), by the reaction of $[RhCl(CO)_2]_2$ with 2,2′-bipyridyl [13] whereas Mestroni, Camus and Zassinovich [14] described this material as a black substance which was formed by the reaction of [Rh(CO)$_3$(bipy)][BF$_4$] with lithium chloride in acetonitrile. However we obtain [RhCl(CO)(bipy)] as a deep purple-red precipitate on addition of bipyridyl to a dichloromethane solution of [RhCl(CO)$_2$]$_2$. The analogous iridium complex [IrCl(CO)(bipy)] (II) can be obtained in a similar manner as a black precipitate when a mixture of [IrCl(C$_8$H$_{14}$)$_2$]$_2$ (C$_8$H$_{14}$ = cyclooctene), and 2,2'-bipyridyl in dichloromethane is exposed to an atmosphere of CO. Both I and II are essentially insoluble in all solvents with which they do not react, and exhibit single CO stretching frequencies (1952 cm^{-1} (Rh) and 1996 cm^{-1} (Ir) (KBr)) although in the latter case the band is rather broad. The deep colours and insolubility of these materials is indicative of the existence of metal–metal interactions.

Although salts of the cation [Rh(bipy)$_2$]$^+$ and [Ir(bipy)$_2$]$^+$ would not be expected to show very strong metal–metal interactions because of the thickness of the aromatic nucleus and contraction of the metal d_{z^2} orbitals by the positive charge some interaction might be expected. No pure species could be isolated from the reaction of [RhCl(C$_6$H$_{10}$)]$_2$ (C$_6$H$_{10}$ = 1,5-hexadiene) or [IrCl(C$_8$H$_{14}$)$_2$]$_2$ with an excess of bipyridyl. However if a solution of [RhCl(C$_6$H$_{10}$)]$_2$ in chloroform is treated with an excess of bipyridyl and then with NaBF$_4$ [Rh(bipy)$_2$][BF$_4$]·CHCl$_3$ (III) is obtained as pale orange crystals. The analogous reaction of [IrCl(C$_8$H$_{14}$)$_2$]$_2$ in dichloromethane however surprisingly gives not the expected [Ir(bipy)$_2$][BF$_4$] but the hydride complex [IrH(bipy)$_2$]·CH$_2$Cl$_2$, (IV), (ν(Ir–H) 2114 cm^{-1}; δ(H) −19.3 ppm). The hydride IV (not the deuteride) is also obtained if the reaction is carried out in CD$_2$Cl$_2$ or if the reagents are pre-wetted with D$_2$O suggesting that the cyclooctene is probably the source of the proton.

[{Rh(C$_6$H$_{10}$)}$_2$(C$_2$O$_4$)] (V) (C$_2$O$_4$$^{2-}$ = oxalate), is readily obtained as a yellow powder by the reaction of [RhCl(C$_6$H$_{10}$)]$_2$ with Ag$_2$C$_2$O$_4$, but the analogous iridium species can not be obtained in significant yields by this method, the iridium apparently remaining bound to be silver salt. However [{(Ir(C$_8$H$_{12}$)}$_2$(C$_2$O$_4$)], (VI), (C$_8$H$_{12}$ = 1,5-cyclohexadiene), may be obtained as an orange powder by treatment of [Ir(acac)(C$_8$H$_{12}$) (acac = acetylacetone) with oxalic acid in acetone.

[{Rh(C$_6$H$_{10}$)}$_2$(C$_2$O$_4$)] forms a simple complex with the phosphinourea ligand O=C(NMePF$_2$)$_2$ [15]. The complex [{Rh(O=C(NMePF$_2$)$_2$}$_2$(C$_2$O$_4$)] (VII) is a rather insoluble orange powder with a ^{31}P{^{1}H} NMR spectrum similar to those described elsewhere by us [12] for rhodium(I) complexes of this ligand (δ(P) 127.5 ppm, ^1J(RhP) 283.2 Hz in dimethylformamide). No pure species could, however, be obtained from the reaction of VI with O=C(NMePF$_2$)$_2$.

Treatment of V with CO in dichloromethane results in the formation of [{Rh(CO)$_2$}$_2$(C$_2$O$_4$)] (VIII) as a purple-red insoluble material. This complex has been prepared independently by Oro, Pinillos, and Jarauta [16,17]. An insoluble blue-black material is also obtained on treatment of [{Ir(C$_8$H$_{12}$)}$_2$(C$_2$O$_4$)] with CO, this material did not give satisfactory microanalyses, but probably consists mainly of [{Ir(CO)$_2$}$_2$(C$_2$O$_4$)]. Both this and the rhodium complex VIII are insoluble in solvents with which they do not react, but dissolve with evolution of CO in CH$_2$Cl$_2$ containing triphenylphosphine.

Experimental

Infrared spectra were recorded on a Perkin–Elmer 1430 spectrometer as KBr discs. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker WP 80 F.T. NMR spectrometer operating at 80 and 32.4 MHz respectively. Microanalyses for C, H, and N were carried out by Mrs. G. Olney of these laboratories.

All reactions were carried out using a combination of Schlenk and high vacuum techniques. Reaction mixtures were usually agitated using an ultrasonic bath. $[IrCl(C_8H_{14})_2]_2$ and $[RhCl(C_6H_{10})]_2$ were prepared by adaptions [18] of the literature methods [19,20].

Chloro(carbonyl)(2,2'bipyridyl)rhodium(I) (I). $[RhCl(CO)_2]_2$ (0.2289 g, 0.589 mmol) was dissolved in dichloromethane and 2,2'-bipyridyl (0.1937 g, 1.275 mmol) was added. After evolution of CO had ceased the purple-red precipitate was filtered off, washed with toluene and dried to give [RhCl(CO)(bipy)] (0.2594 g, 63.5%). Analytical data for this and other complexes are listed in Table 1.

Chloro(carbonyl)(2,2'bipyridyl)iridium(I) (II). $[IrCl(C_8H_{14})_2]_2$ (0.0814 g, 0.09 mmol) and 2,2'-bipyridyl (0.0453 g, 0.1901 mmol) were dissolved in dichloromethane. The red mixture was filtered then stirred overnight under an atmosphere of CO. The resultant black precipitate was filtered and washed with toluene to give [IrCl(CO)(bipy)] (0.0695 g, 92.7%).

Bis(2,2'-bipyridyl)rhodium(I)tetrafluoroborate (III). $[RhCl(C_6H_{10})]_2$ (0.0942 g, 0.214 mmol) and 2,2'-bipyridyl (0.1248 g, 0.799 mmol) were dissolved in chloroform. A large excess of $NaBF_4$ (0.2109 g, 1.921 mmol) was added and the solution was agitated for 2 h, filtered, and a layer of petroleum ether floated on top. After 18 h large feathery crystals of $[Rh(bipy)_2][BF_4] \cdot CHCl_3$ (0.0815 g, 32.8%) were obtained.

Hydridobis(2,2'-bipyridyl)iridium(I) (IV). $[IrCl(C_8H_{14})_2]_2$ (0.1398 g; 0.156 mmol) and 2,2'-bipyridyl (0.1466 g, 0.939 mmol) were dissolved in CH_2Cl_2 to give a red solution which was shaken with solid $NaBF_4$ (0.4338 g, 3.951 mmol) for 2 h. The solution was filtered and a layer of petroleum ether floated on top. After 18 h a red somewhat oily product was obtained. Repeated recrystallisation from CH_2Cl_2/petroleum ether yields yellow $[IrH(bipy)_2] \cdot CH_2Cl_2$ (0.0894 g, 48.5%).

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES I–VIII

Complex	Mol.form.	Analysis (found (calcd.)(%))		
		C	H	N
[RhCl(CO)(bipy)] (I)	$C_{11}H_8ClN_2ORh$	41.06	2.51	8.48
		(40.96)	(2.50)	(8.68)
[IrCl(CO)(bipy)] (II)	$C_{11}H_8ClIrN_2O$	31.67	2.29	6.00
		(32.08)	(1.96)	(6.80)
$[Rh(bipy)_2][BF_4] \cdot CHCl_3$ (III)	$C_{21}H_{17}BCl_3F_4N_4Rh$	40.74	3.22	8.76
		(40.59)	(2.76)	(9.02)
$[IrH(bipy)_2] \cdot CH_2Cl_2$ (IV)	$C_{21}H_{19}Cl_2IrN_4$	42.23	3.34	9.40
		(42.71)	(3.24)	(9.49)
$[\{Rh(C_6H_{10})\}_2(C_2O_4)]$ (V)	$C_{14}H_{20}O_4Rh_2$	35.16	4.05	–
		(36.71)	(4.40)	
$[\{Ir(C_8H_{12})\}_2(C_2O_4)]$ (VI)	$C_{18}H_{24}Ir_2O_4$	31.73	3.70	–
		(31.39)	(3.51)	
$[\{Rh(O{=}C(NMePF_2)_2\}_2(C_2O_4)]$ (VII)	$C_{16}H_{12}F_8N_4O_6P_4Rh_2$	11.76	1.72	8.04
		(12.95)	(1.63)	(7.55)
$[\{Rh(CO)_2\}_2(C_2O_4)]$ (VIII)	$C_6O_8Rh_2$	17.54	–	–
		(17.76)		

Oxalatobis(1,5-hexadiene)dirhodium(I) (V). $[RhCl(C_6H_{10})]_2$ (0.3781 g, 0.857 mmol) was dissolved in diethyl ether and stirred with $Ag_2C_2O_4$ (0.808 g, 2.660 mmol) for 20 h. The solution was filtered and dried to yield $[\{Rh(C_6H_{10})\}_2(C_2O_4)]$ (0.3519 g, 89.6%).

Oxalatobis(1,5-cyclooctadiene)diiridium(I) (VI). $[IrCl(C_8H_{14})_2]_2$ (0.1108 g, 0.124 mmol) was treated with acetylacetone (0.30 ml, 2.9 mmol), triethylamine (0.30 ml, 2.2 mmol) and 1,5-cyclohexadiene (0.30 ml, 2.4 mmol) in toluene (4 ml). After 3 h the solution was filtered to remove NEt_3HCl and dried. The acetylacetonate was not purified, but was dissolved directly in acetone (5 ml) and a solution of anhydrous oxalic acid (0.115 g, 1.283 mmol) in acetone (4 ml) was added. After a few minutes an orange precipitate started to form. After 3 h the volume was reduced under vacuum to ca. 4 ml, the product filtered off, washed with acetone, methanol, and dried to give $[\{Ir(C_8H_{12})\}_2(C_2O_4)]$ (0.0256 g, 59.9%).

Oxalatobis(N,N'-dimethyl-N,N'-bisdifluorophosphinourea)dirhodium(I) (VII). A solution of $O{=}C(NMePF_2)_2$ (0.6 ml, 0.1726 g ml^{-1}, 0.46 mmol) was added to $[\{Rh(C_6H_{10})\}_2(C_2O_4)]$ (0.0794 g, 0.173 mmol) in dichloromethane (1.0 ml). An orange precipitate immediately started to form. After 30 min the solvent was removed in vacuo and the orange residue was washed several times with petroleum ether to give $[\{Rh(O{=}C(NMePF_2)_2\}_2(C_2O_4)]$ (0.1027 g, 79.9%).

Oxalatotetracarbonyldirhodium(I) (VIII). $[\{Rh(C_6H_{10})\}_2(C_2O_4)]$ (0.2195 g, 0.479 mmol) was dissolved in CH_2Cl_2 (5 ml) and stirred in an atmosphere of CO for 18 h. The purple-red precipitate was filtered off, washed with toluene and dried to give $[\{Rh(CO)_2\}_2(C_2O_2)]$ (0.1738 g, 89.4%).

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