

inductive electron withdrawal from the CO_3^{2-} ligand by the cobalt.

A possibly more direct measure of the effect of the amine ligand may be gained from the $\text{p}K_a$ values of the aquo species, $\text{N}_4\text{Co}(\text{OH}_2)_2^{3+}$. The more strongly electron-donating amines should make the coordinated water molecule less acidic. These $\text{p}K_a$ values also are given in Table VI and generally show the expected trend with amine $\text{p}K$ and hydrolysis rate. It is concluded from these correlations that the electron-donor variations of the amines are much more important than steric effects in explaining the large variation in the acid hydrolysis rate constants (k_1) for the $\text{N}_4\text{CoCO}_3^+$ systems.

It has been proposed by Gatehouse, *et al.*,²⁷ that the $\text{C}=\text{O}$ stretching frequency in chelated carbonate complexes might be used as a measure of the $\text{M}-\text{O}$ bond energy, a higher stretching frequency correlating with a stronger $\text{M}-\text{O}$ bond. This correlation has been applied recently by Farago, Keefe, and Mason²⁸ to the $(\text{phen})_2\text{CoCO}_3^+$ complex which has $\nu(\text{C}=\text{O})$ 1650 cm^{-1} compared to 1613 and 1593 cm^{-1} in $(\text{en})_2\text{CoCO}_3^+$ and $(\text{NH}_3)_4\text{CoCO}_3^+$, respectively. A value of 1632 cm^{-1} has been observed in our work for $(\text{bipy})_2\text{CoCO}_3^+$,

(27) B. M. Gatehouse, S. E. Livingston, and R. S. Nyholm, *J. Chem. Soc.*, (1958).

(28) M. E. Farago, I. M. Keefe, and C. F. V. Mason, *ibid.*, A, 3194 (1970).

and Endicott, *et al.*,²⁹ give values of 1665 and 1597 cm^{-1} for the *trans*[14]diene and *tetb* complexes. Comparison of the $\nu(\text{C}=\text{O})$ values and rate constants (k_1) shows that a qualitative correlation does exist except for the *tetb* complex. The larger ΔH_2^\ddagger of $(\text{NH}_3)_4\text{CoCO}_3^+$ compared to that of $(\text{en})_2\text{CoCO}_3^+$ and of $(\text{bipy})_2\text{CoCO}_3^+$ compared to that of $(\text{phen})_2\text{CoCO}_3^+$ would not be anticipated from the $\nu(\text{C}=\text{O})$ values however. Also the compilation of $\nu(\text{C}=\text{O})$ values in ref 1 shows that the value is affected by anion and hydrogen-bonding effects and that *trans*- $(\text{NH}_3)_2\text{enCoCO}_3^+$ and *trienCoCO}_3^+ complexes do not conform to the expectations of Farago, *et al.**

Although the k_0 values determined here are quite inaccurate, they do provide an upper limit which indicates that k_0 is $\sim 10^2$ times smaller in the $(\text{phen})_2\text{CoCO}_3^+$ and $(\text{bipy})_2\text{CoCO}_3^+$ systems than in the more normal cases such as $(\text{en})_2\text{CoCO}_3^+$. It appears that the k_0 values roughly parallel the k_1 values. This implies that the k_0 path also proceeds with $\text{Co}-\text{O}$ bond breaking, a point which has yet to be established. The greater sensitivity of k_1 to changes in the amine ligands may be rationalized if it is assumed that both the protonation equilibrium (eq 6) and bond breaking are involved in the k_1 path, but only bond breaking will be important for the k_0 path.

(29) N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, **6**, 770 (1967).

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Iridium(I) and Iridium(III) Complexes with *cis*-Vinylenebis(diphenylphosphine)

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The preparation of new four- and five-coordinated complexes of iridium(I) and six-coordinated complexes of iridium(III) with *cis*-vinylenebis(diphenylphosphine) (dp) is reported. The properties of the compounds are discussed with regard to the presence of the double bond in the dp ligand, which results in a better π acceptor than 1,2-bis(diphenylphosphino)ethane (DP).

Introduction

It is well known that several transition metal complexes having particularly "soft" ligands are apt to coordinate small molecules, such as H_2 , O_2 , CO , etc., in a reversible way. Some new useful complexes in this regard are those of formula $[\text{IrY}(\text{dp})_2]\text{X}$ ($\text{Y} = \text{CO}$, H_2 , O_2 , HCl , HBr , HI ; $\text{X} = \text{Cl}$, Br , I , ClO_4 , BPh_4 ; $\text{dp} = \textit{cis}$ -vinylenebis(diphenylphosphine), $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$) and $[\text{Ir}(\text{dp})_2]\text{X}$, which we have recently synthesized. These chelate complexes behave somewhat differently from the analogous compounds containing the saturated diphosphine-1,2-bis(diphenylphosphino)ethane $\text{C}_2\text{H}_4(\text{PPh}_2)_2$ (DP).¹ This different behavior is attributed to the double bond present in the dp ligand.

Experimental Section

All reactions were carried out under a nitrogen atmosphere.

(1) L. Vaska and D. L. Catone, *J. Amer. Chem. Soc.*, **88**, 5324 (1966).

Infrared spectra were obtained with a Perkin-Elmer spectrometer Model 337. Melting points are uncorrected. Analytical data are reported in Table I. Infrared spectral data are reported in Table II. The diphosphine was prepared previously as reported.²

Carbonylbis(*cis*-vinylenebis(diphenylphosphine))iridium(I) Chloride, $[\text{Ir}(\text{CO})\{\text{C}_2\text{H}_2(\text{Ph}_2\text{P})_2\}_2]\text{Cl}$.—(a) A solution of $[\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2]$ (1.37 g, 1.75 mmol) in degassed benzene (120 ml) was treated, under stirring, with a solution of dp (1.45 g, 3.66 mmol) in benzene (5 ml). The mixture was stirred for several hours. The yellow-green precipitate was filtered, washed with benzene, and crystallized from acetone-benzene (2:1) in petroleum ether (bp 60–80°).

(b) An acetone-benzene solution of $[\text{Ir}\{\text{C}_2\text{H}_2(\text{Ph}_2\text{P})_2\}_2]\text{Cl}$ was saturated with carbon monoxide. The reaction occurred instantaneously and the carbonyl compound was precipitated by addition of petroleum ether. If $[\text{Ir}(\text{dp})_2]\text{Cl}$ was allowed to react in the solid state with carbon monoxide, its conversion to carbonyl compound was very slow, but complete within 10 days. The corresponding carbonyl bromide, iodide, perchlorate, and tetraphenylborate complexes were obtained from the chloride by exchange with the appropriate salt in water-ethanol solution.

(2) A. M. Aguiar and D. J. Daigle, *ibid.*, **86**, 2299 (1964).

TABLE I
ANALYTICAL DATA FOR COMPLEXES

No.	Complex	Color	Mp, °C	Analyses, %							
				C		H		P		Halogen	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
1	[Ir(CO)(dp) ₂]Cl	Yellow-green	160-180 dec	60.71	60.67	4.22	4.15	11.82	11.75	3.38	3.40
2	[Ir(CO)(dp) ₂]Br	Yellow-green	155-170 dec	58.24	58.65	4.05	3.98	11.34	11.20	7.31	7.38
3	[Ir(CO)(dp) ₂]I	Yellow-green	150-170 dec	55.84	55.63	3.89	4.00	10.87	10.79	11.13	11.30
4	[Ir(CO)(dp) ₂]ClO ₄	Yellow	155-180 dec	57.19	57.70	3.98	4.00	11.14	11.32	3.19	3.10
5	[Ir(CO)(dp) ₂]BPh ₄	Yellow	140-160 dec	69.39	69.20	4.84	4.71	9.31	9.40		
6	[Ir(dp) ₂]Cl	Orange	328-329 dec	61.17	61.00	4.34	4.30	12.15	12.29	3.48	3.50
7	[Ir(dp) ₂]Br	Orange	330-332 dec	58.68	59.10	4.16	4.10	11.64	11.52	7.50	7.53
8	[Ir(dp) ₂]I	Orange	332-334 dec	56.14	55.80	3.99	4.13	11.16	11.19	11.42	11.53
9	[Ir(dp) ₂]ClO ₄	Yellow-orange	280-283 dec	57.56	57.81	4.09	3.88	11.43	10.98	3.27	3.30
10	[Ir(dp) ₂]BPh ₄	Yellow-orange	285-288 dec	69.96	70.20	4.94	5.03	9.72	9.60		
11	[IrH ₂ (dp) ₂]Cl	White	160-162 dec	61.05	59.80	4.53	5.00	12.12	11.98	3.47	3.46
12	[IrH ₂ (dp) ₂]Br	White	160-163 dec	58.51	59.32	4.34	4.28	11.61	11.73	7.49	7.50
13	[IrH ₂ (dp) ₂]I	White-cream	182-185 dec	56.04	57.03	4.16	3.99	11.12	11.25	11.39	11.20
14	[IrH ₂ (dp) ₂]ClO ₄	White	155-158 dec	57.45	57.32	4.26	4.12	11.41	11.30	3.26	3.28
15	[IrH ₂ (dp) ₂]BPh ₄	White	180-184 dec	69.85	70.00	5.09	5.23	9.49	9.29		
16	[IrHCl(dp) ₂]Cl	White	270-272 dec	59.05	59.44	4.29	4.13	11.72	11.93	6.71	6.66
17	[IrHCl(dp) ₂]ClO ₄	White	290-292 dec	55.68	55.71	4.04	3.98	11.06	10.85	6.33	6.31
18	[IrHCl(dp) ₂]BPh ₄	White	245-248 dec	68.61	68.50	3.96	4.01	9.24	9.29	2.64	2.65
19	[IrHBr(dp) ₂]Br	White	340-342 dec	54.47	55.13	4.92	4.76	10.81	11.04	13.95	13.81
20	[IrHBr(dp) ₂]ClO ₄	White	307-310 dec	53.56	54.06	3.89	3.78	10.64	9.98	3.04	3.10
										(Cl)	(Cl)
										6.86	6.78
										(Br)	(Br)
21	[IrHBr(dp) ₂]BPh ₄	White	245-249 dec	65.87	64.13	4.73	5.01	8.95	8.89	5.77	5.66
22	[IrHI(dp) ₂]I	White-cream	345-350 dec	50.34	51.00	3.65	3.45	9.99	9.82	20.47	20.58
23	[IrHI(dp) ₂]ClO ₄	White-cream	310-313 dec	51.48	51.12	3.74	3.52	10.13	9.98	3.08	3.10
										(Cl)	(Cl)
										10.47	10.33
										(I)	(I)
24	[IrHI(dp) ₂]BPh ₄	White-cream	216-221 dec	63.71	64.22	4.57	4.61	8.65	8.70	8.87	8.80
25	[IrO ₂ (dp) ₂]Cl	White-cream	150-160 dec	59.31	60.13	4.21	4.12	11.78	11.70	3.37	3.38

^a Determined in evacuated tubes.

TABLE II
INFRARED SPECTRAL DATA

Complex	ν_{C-O} , ^a cm ⁻¹	Complex	ν_{Ir-H} , ^a cm ⁻¹
1	1955 vs	11	2080 ms, 2060 s
2	1955 vs	12	2080 ms, 2060 s
3	1955 vs	13	2080 ms, 2060 s
4	1965 vs	14	2085 ms, 2065 s
5	1950 vs	15	2085 ms, 2065 s
		16	2218 m
		17	2200 m
		18	2169 m
		19	2208 m
		20	2208 m
		21	2190 m
		22	2187 m
		23	2187 m
		24	2180 m

^a Nujol mulls. Abbreviations: m, medium; s, strong; ms, medium strong; vs, very strong.

Bis(*cis*-vinylenebis(diphenylphosphine))iridium(I) Chloride, [Ir{C₂H₂(Ph₂P)₂]₂]Cl.—(a) The crystalline carbonyl complex [Ir(CO)(dp)₂]Cl was heated on an oil bath at 160-180° under reduced pressure (0.1 mm) for 3 hr; the decarbonylation was accompanied by the appearance of an orange color and was checked by means of infrared spectrometry for the disappearance of the CO band.

(b) A suspension of white [IrHCl{C₂H₂(Ph₂P)₂]₂]Cl (0.52 g, 0.49 mmol) in aqueous (80%) ethanol (10 ml) was treated with 5 ml of water-alcohol (4:1) KOH solution (0.1 M); the color slowly changed to orange. The filtered product, washed with degassed water and dried, was identified by its ir spectrum and elemental analyses.³

Dihydrido(*cis*-vinylenebis(diphenylphosphine))iridium(III) Chloride, [IrH₂{C₂H₂(Ph₂P)₂]₂]Cl.—(a) The complex was prepared by reaction of molecular hydrogen with [Ir(dp)₂]Cl either in the crystalline state (slow reaction) or in solution (rapid reaction); a white crystalline product was obtained.

(b) The corresponding compounds with heavier ClO₄⁻ and BPh₄⁻ anions were obtained in a similar way or by metathetic exchange.

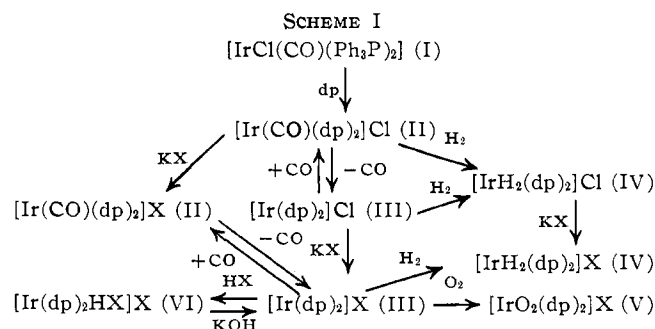
(b) A yellow-green acetone-benzene solution (10 ml) of the carbonyl compound [Ir(CO)(dp)₂]Cl (0.3 g) was saturated with molecular hydrogen. Discoloration occurred slowly and the solution became colorless within 5 hr. By adding petroleum ether, the white product was precipitated and recognized by its ir spectrum.³

Hyridochlorobis(*cis*-vinylenebis(diphenylphosphine))iridium(III) Chloride, [IrHCl{C₂H₂(Ph₂P)₂]₂]Cl.—A 4.9-ml sample of 0.1 M aqueous HCl was added to a solution of [Ir(dp)₂]Cl (0.5 g, 0.49 mmol) in ethanol (4 ml); a rapid discoloration occurred accompanied by an initial precipitation, which was completed on cooling the solution. The white crystalline product was collected and dried under vacuum. The complexes [Ir(dp)₂HBr]Br and [Ir(dp)₂HI]I were prepared in a similar way, starting from the appropriate compounds and halogen acid solution.³

Peroxis(*cis*-vinylenebis(diphenylphosphine))iridium(I) Chloride, [IrO₂{C₂H₂(Ph₂P)₂]₂]Cl.—When an acetone-benzene solution of [Ir(dp)₂]Cl was saturated with oxygen, a slow decoloration occurred. From the cream-colored solution the oxygen adduct was precipitated by addition of petroleum ether and was collected and dried under vacuum.

Results and Discussion

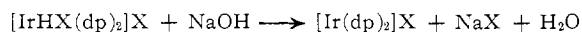
From the well-known Vaska compound (I) (Scheme I) a considerably air-stable, five-coordinated carbon



monoxide adduct $[\text{Ir}(\text{CO})(\text{dp})_2]\text{X}$ (II) has been obtained, similarly to the analogous compound with 1,2-bis(diphenylphosphino)ethane (DP).^{1,4} From II, by loss of CO either in solution or in the solid state (160–180°, 0.1 mm), the four-coordinated diphosphine chelate $[\text{Ir}(\text{dp})_2]\text{X}$ (III) was formed, the carbonylation being reversible under mild conditions. The ir spectrum of II (Table II) shows a strong band in the 1950–1965- cm^{-1} range, characteristic of the coordinated CO group. The observed frequency shift with respect to the analogous complex with DP (ν_{CO} 1933 cm^{-1})¹ indicates a higher CO bond order and may be related to the back-donation from the metal to the phosphine ligands and the CO group. In fact, the tendency of the dp ligand to favor electron delocalization, due to the presence of the double bond, leads to a lowering of its basicity and to a π -bonding ability higher than that of the DP ligand. Therefore the DP makes less demand for the $d\pi$ electrons of the metal, and the back-donation involves mainly the CO group.

The displacement reaction of CO from $[\text{IrCO}(\text{dp})_2]\text{Cl}$ by means of molecular hydrogen, which gives the dihydrido complex $[\text{IrH}_2(\text{dp})_2]\text{X}$ (IV) (Scheme I), takes place slowly and only in solution, whereas for the corresponding CO-DP complex this displacement reaction occurs also in the crystalline state,⁵ although slowly. One therefore can say that the dp complexes are more stable than the corresponding complexes of DP, and this is also confirmed by the respective thermal behavior and by other differences in their properties. For example, complex III is sufficiently air stable (no reaction with atmospheric oxygen in 10 days), and the oxygen adduct $[\text{IrO}_2(\text{dp})_2]\text{X}$ (V) ($\nu_{\text{Ir}-\text{O}_2}$ 843 cm^{-1}) was slowly obtained (ca. 2 hr) only in solution, whereas the analogous DP compound reacts with oxygen both in the solid state (slowly) and in solution (within minutes).^{1,5} The peroxo compound (V) also shows a considerable stability with respect to the corresponding $[\text{IrO}_2(\text{DP})_2]\text{X}$. In fact this latter slowly undergoes substitution of O_2 from H_2 , on standing in hydrogen atmosphere even in the crystalline state, to give the dihydrido complex,⁵ while the corresponding dihydrido

complex (IV) was not obtained from the former (V) under any conditions. $[\text{Ir}(\text{dp})_2]\text{X}$ (III) readily adds hydrogen, either in the crystalline state at room temperature and atmospheric pressure or in solution, to give the dihydrido complex $[\text{IrH}_2(\text{dp})_2]\text{X}$ (IV); the Ir-H stretching frequencies (Table II) suggest that the two hydrogens occupy cis positions. Finally, compounds III behave as Lewis bases with halogen acids similarly to the analogous complex with DP.^{1,4-6} The resulting products are the air-stable, six-coordinated adducts $[\text{IrHX}(\text{dp})_2]\text{X}$ (VI), which show the Ir-H stretching frequency in the range $2200 \pm 20 \text{ cm}^{-1}$ (Table II). From these iridium(III) hydrido complexes it is possible to obtain again the iridium(I) complex III by dehydrohalogenation with alkali in aqueous-alcoholic solution, according to the schematic equation



All these five- and six-coordinated complexes behave as uni-univalent electrolytes (Λ_{M} 20–30 $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in nitrobenzene solution 10^{-3} M at 25°) and their ionic character was confirmed by the replacement of the chloride with heavier ClO_4^- and BPh_4^- anions.

Conclusions

The results of this study show that in some cases the complexes of *cis*-vinylenebis(diphenylphosphine) (dp) behave differently from the corresponding compounds of 1,2-bis(diphenylphosphino)ethane (DP). The dp and DP ligands have similar coordinating ability toward Ir(I) and Ir(III), as far as coordination number and stereochemistry are concerned. However, the dp ligand is less apt than DP in the replacement of Ph_3P from Vaska's complex (the reaction, in benzene solution, being much slower than with DP). On the other hand, the unsaturated dp ligand is more effective in the delocalization of the $d\pi$ electrons of the metal, and its chelate complexes are more stable than the corresponding complexes of the saturated DP ligand.

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(4) A. Sacco, M. Rossi, and C. F. Nobile, *Chem. Commun.*, 589 (1966).
 (5) A. Sacco, S. Doronzo, and L. Uva, unpublished work.

(6) A. Sacco, *Euchem Hydride Conference*, Bristol, England, April 1966.