Our kinetic data do not distinguish between these two mechanistic variants which become equivalent if, as is indeed expected to be the case, the intermediate of the first mechanism, $[(NC)_5FeCN(CN)_5]^{7-}$, dissociates rapidly into $Fe(CN)_6^{4-}$ and $Co(CN)_5^{3-}$. The nature of the ionic strength dependence and the large negative $\Delta S^{\ddagger}$ are consistent with the proposed rate-determining step between two negative ions.

Our value of k_5 ($8.1 \times 10^{-2}\ M^{-1}\ sec^{-1}$ at 25°, $\mu = 0.5\ M$) is in reasonably good agreement with the corresponding value ($9.6 \times 10^{-2}\ M^{-1}\ sec^{-1}$ at 24°, $\mu = 0.5\ M$ adjusted with $NaClO_4$ instead of KCl) determined by Lim and Anson[4] from kinetic measurements on the reaction of $Co(CN)_5H^{3-}$ with $Hg(CN)_2$. However, as already pointed out by Lim and Anson,[4] this value is too low to accommodate a mechanism encompassing eq 5 as a step, such as that proposed by Hanzlik and Vlcek,[3] for the much faster reaction of $Co(CN)_5H^{3-}$ with benzoquinone. The origin of this discrepancy is unclear and warrants further investigation.

In contrast to the reaction with $Hg(CN)_2$[4], the reaction of $Co(CN)_5^{4-}$ with $Fe(CN)_6^{3-}$ (eq 6a or 7a) is too fast for significant competition from the back-reaction of eq 5 (*i.e.*, from eq 8) to be observed even at our lowest $Fe(CN)_6^{3-}$ concentrations (*ca.* $1.8 \times 10^{-4}\ M$). Since, based on an earlier direct determination,[7] $k_{-5} = 1.1 \times 10^5\ sec^{-1}$, we conclude that the rate constant for the reaction of $Co(CN)_5^{4-}$ with $Fe(CN)_6^{3-}$ (eq 6a or 7a) must be at least $10^{10}\ M^{-1}\ sec^{-1}$, *i.e.*, essentially diffusion controlled. Combination of the values

$$Co(CN)_5^{4-} + H_2O \xrightarrow{k_{-5}} Co(CN)_5H^{3-} + OH^- \qquad (8)$$

k_5 and k_{-5}, cited above, yields a value of about 20 for the pK_a of $Co(CN)_5H^{3-}$ which, thus, is an extremely weak acid.

Acknowledgments.—Support of this work through grants from the National Institutes of Health and from the National Science Foundation is gratefully acknowledged. M. P. also thanks the U. S. Government Fulbright–Hays Program for a travel grant and the University of Zagreb for a leave of absence.

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Hydridocarboxylato Complexes of Iridium

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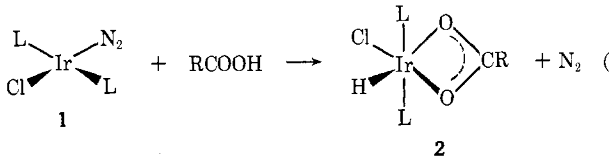
Received July 12, 1971

The formation of hydrido–transition metal complexes by the oxidative addition of protonic acids to complexes of transition metals in low oxidation states is relevant to the elucidation of fundamental processes involved in reactions which are homogeneously catalyzed.[2] The oxidative addition of hydrogen halides HX to square-planar d^8 complexes *trans*-$Ir(CO)X(P(C_6H_5)_3)_2$ leads to formation of the hydrido complexes $IrH(CO)X_2(P(C_6H_5)_3)_2$.[3] While it is expected that carboxylic acids, RCOOH, should form hydridocarboxylato complexes, $IrH(CO)X(RCOO)(P(C_6H_5)_3)_2$, such complexes have not been isolated except for acids in which R is CF_3 or C_2F_5.[4] The formation of hydrido complexes by oxidative addition of protonic acids to d^{10} complexes is observed when the acid is strong or when the conjugate base of the acid is a good ligand.[5] The extent of protonation of four-coordinated iridium(I) complexes by carboxylic acids has been related to the basicity of the iridium complex and the pK_a of the carboxylic acid.[6] Due to extensive dissociation, the carboxylatohydrido complexes have not been isolated. That the carboxylato group is a good ligand for iridium(III) is indicated by the isolation of complexes formed by substitution of the chloro ligands using silver carboxylates.[7] Details for the synthesis of these compounds have not been presented. Carboxylato ligands form strong bonds in related complexes. For example, monodentate carboxylato complexes are formed in oxidative addition reactions of carboxylic acids with d^8 complexes of ruthenium.[8] These reactions, however, do not form hydrido derivatives. Hydridocarboxylatotris(triphenylphosphine)ruthenium(II) complexes have been prepared by the reactions of $RuCl_2(P(C_6H_5)_3)_3$, the sodium salt of a carboxylic acid, and hydrogen in methanol.[9]

Carboxylic acids have been found in the present study to react with *trans*-$IrCl(N_2)(P(C_6H_5)_3)_2$ to form hydridocarboxylato complexes **2** (L is triphenylphosphine).



(1)

Analytical results for all compounds are given in Table I. Pertinent ir spectral data for these complexes are presented in Table II. The Ir–H stretching frequencies in the 2221–2304-cm^{-1} region are much higher than those in related iridium(III) hydrido complexes[10] or related ruthenium(II) hydridocarboxylato complexes.[9] The high frequencies may be attributed to the low trans labilizing properties of the carboxylato ligand. The assignment of the Ir–H stretching frequencies was confirmed by running a reaction of the dinitrogen complex **1** with deuterioacetic acid. The product **2A′** has a band at 1655 cm^{-1} which is assigned to the Ir–D stretching frequency ($\nu(Ir\text{–}H)/\nu(Ir\text{–}D) = 1.392$). The far-ir data in the Ir–Cl stretching region, namely, the absence of absorption in the 250–275-cm^{-1} region, indicate that Cl is not trans to a hydrido or triphenylphosphine ligand.[10] The symmetric and asymmetric carboxylato frequencies in the

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TABLE I
ANALYTICAL RESULTS

No.	Compound	% C		% H		% Cl		Mp, °C[a]
		Calcd	Found	Calcd	Found	Calcd	Found	
2A	$IrClH(P(C_6H_5)_3)_2CH_3CO_2$	56.2	56.3	4.22	4.36	4.36	4.40	187–189
2B	$IrClH(P(C_6H_5)_3)_2C_2H_5CO_2$	56.7	56.5	4.39	4.53	4.29	3.58	
2C	$IrClH(P(C_6H_5)_3)_2C_3H_7CO_2$	57.1	57.0	4.55	4.58	4.21	4.44	169–172
2D	$IrClH(P(C_6H_5)_3)_2C_6H_5CO_2$[b]	61.4	61.8	4.40	4.44	3.80	3.72	156–161
2E	$IrClH(P(C_6H_5)_3)_2HCO_2$	55.7	56.0	4.04	4.33	4.44	4.35	161–164
2F	$IrClH(P(C_6H_5)_3)_2CF_3CO_2$	52.7	52.6	3.61	3.79	4.09	4.05	136–141
3A	$IrCl(CO)H(P(C_6H_5)_3)_2CH_3CO_2$	55.7	55.8	4.08	4.27	4.22	3.91	235–245
3B	$IrCl(CO)H(P(C_6H_5)_3)_2C_2H_5CO_2$	56.2	57.2	4.25	4.32	4.15	4.15	228–235
3D	$IrCl(CO)H(P(C_6H_5)_3)_2C_6H_5CO_2$	60.2	58.6	4.48	4.02	3.90	3.93	260–269
3E	$IrCl(CO)H(P(C_6H_5)_3)_2HCO_2$	55.2	56.0	3.90	4.03	4.29	4.32	235–245
3F	$IrCl(CO)H(P(C_6H_5)_3)_2CF_3CO_2$	52.4	52.6	3.49	3.45	3.96	4.18	
4A	$IrCl(C_5H_5N)H(P(C_6H_5)_3)_2CH_3CO_2$	57.9	57.8	4.41	4.38	1.57	1.50	157–161
4B	$IrCl(C_5H_5N)H(P(C_6H_5)_3)_2C_2H_5CO_2$	58.4	58.0	4.57	4.49	1.55	1.33	150–154
5C	$IrCl(C_6H_5CN)H(P(C_6H_5)_3)_2C_3H_7CO_2$	59.8	57.7	4.59	4.55	1.53	1.12	
6D	$IrCl(P(CH_3)_2C_6H_5)H(P(C_6H_5)_3)_2C_6H_5CO_2$	63.4	62.6	4.77	4.59	3.51	3.29	151–148
7A	$IrCl(p\text{-}CH_3C_6H_4NC)H(P(C_6H_5)_3)_2CH_3CO_2$	59.4	58.7	4.55	4.49	1.51[c]	1.72[c]	

[a] Compounds decomposed upon melting. [b] Contains one molecule of benzene. [c] Analysis for nitrogen.

TABLE II
INFRARED SPECTRAL DATA (CM^{-1}) FOR CHLOROHYDRIDOCARBOXYLATOBIS(TRIPHENYLPHOSPHINE)-IRIDIUM(III), **2**

No.	R	$\nu(CO_2)_{asym}$	$\nu(CO_2)_{sym}$	ν-(Ir–Cl)	ν(Ir–H)
2A	CH_3	1535	1445, 1423, 1412	319	2304
2B	C_2H_5	1525	1438	313	2293
2C	C_3H_7	1530	1408	313	2293
2D	C_6H_5	1520	1418, 1401	315	2242
2E	H	1550	1345, 1279	320	2304
2F	CF_3	1710, 1680	1410	338	2221
2G	CH_3CHCl	1547	1410	318	2271
2H	$p\text{-}O_2NC_6H_4$	1534[b]	1420	318	2268
2A′	CH_3	1535	1338	318	1655[a]

[a] Ir–D stretching frequency for product obtained from deuterioacetic acid. [b] NO_2 absorption at 1513 cm^{-1}.

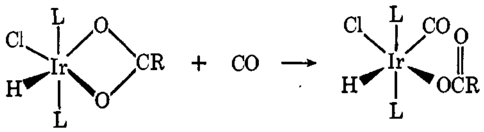
TABLE III
INFRARED SPECTRAL DATA (CM^{-1}) FOR PRODUCTS OBTAINED UPON ADDITION OF CARBON MONOXIDE AND OTHER NUCLEOPHILES TO THE CARBOXYLATO COMPLEXES **2** (L IS $P(C_6H_5)_3$)

No.	Compound	$\nu(CO_2)_{asym}$	$\nu(CO_2)_{sym}$	ν(Ir–Cl)	ν(Ir–H)	ν(CO)
3A	$IrClHL_2(CO)CH_3CO_2$	1631, 1613	1310	315	2135	2026
3A′	$IrClDL_2(CO)CH_3CO_2$	1634, 1618 sh	1311, 1351	316	*a*	2060
3B	$IrClHL_2(CO)C_2H_5CO_2$	1626	1325	320	2115	2010 2018 sh
3C	$IrClHL_2(CO)C_3H_7CO_2$	1622	1335	311	2145	2035
3D	$IrClHL_2(CO)C_6H_5CO_2$	1621, 1612	1338	315	2145	2025
3E	$IrClHL_2(CO)HCO_2$	1687	1362	318	2145	2036
3F	$IrClHL_2(CO)CF_3CO_2$	1654	1330	312	2100	2005
3G	$IrClHL_2(CO)CH_3CHClCO_2$	1632	1272	318	2120, 2105 sh	2025
4A	$IrClHL_2(C_5H_5N)CH_3CO_2$	1636	1355	309	2254	
4B	$IrClHL_2(C_5H_5N)C_2H_5CO_2$	1636	1356	306	2269	
4D	$IrClHL_2(C_5H_5N)C_6H_5CO_2$	1632	1320	310	2256	
5A	$IrClHL_2(C_6H_5CN)CH_3CO_2$	1639	1354	315, 304	2201[b]	
5C	$IrClHL_2(C_6H_5CN)C_3H_7CO_2$	1626	1355	310	2238[c]	
6D	$IrClHL_2(P(CH_3)_2(C_6H_5))C_6H_5CO_2$	1630	1323	316	2242	
7A	$IrClHL_2(p\text{-}CH_3C_6H_4NC)CH_3CO_2$	1630	1352	308	2180[d]	

[a] Ir–D frequency is obscured by strong carboxylate absorption. [b] ν(CN) at 2247 cm^{-1}. [c] ν(CN) at 2279 cm^{-1}. [d] Strong ν(NC) absorption is also observed in this region (2175–2185 cm^{-1}).

1530- and 1410-cm^{-1} regions are diagnostic of chelated carboxylato ligands. Similar spectral characteristics were noted for bidentate carboxylatoruthenium complexes.[9]

Carbonylation of the bidentate carboxylato complexes **2** leads to formation of the hydridocarbonyl complexes **3**. Pertinent ir spectral data for these complexes are shown in Table III. Upon carbonylation, significant changes are observed in the carboxylato region of the infrared spectra reflecting the conversion of the carboxylato group from a bidentate to a monodentate ligand. The frequencies in the 1610–1650- and 1310–1338-cm^{-1} regions which are assigned to carboxylato absorption compare favorably with frequencies assigned to monodentate carboxylato ligands in related complexes.[8] The Ir–Cl stretching frequencies for the hydridocarbonyl complexes **3** in the 311–320-cm^{-1} region are in the same range observed for the monodentate carboxylato complexes **2** in which the Cl ligand is trans to a carboxylato oxygen atom, but this alone does not exclude structures in which the Cl ligand is trans to CO.[10] As mentioned previously, structures for **3** with Cl trans to L or Cl trans to H can be excluded because of absence of absorption in the 250–275-cm^{-1} region. The Ir–H stretching frequencies observed in the 2100–2145-cm^{-1} region for the hydridocarbonyl complexes **3** are significantly lower than those observed for the corresponding carboxylato complexes **2**. Such lowering may be attributed to the trans labilization by the carbonyl ligand.[10b] The trans H-Ir-CO structure depicted for compound **3** is also supported by the observation of hydridocarbonyl vibra-



2 **3**

(2)

tional coupling.[11] The stereochemical course of the carbonylation in reaction 2 is thus directed to a site trans to the strongly trans-directing hydrido ligand. The hydridocarboxylato complexes **3** are isomers of the products expected in the oxidative addition of carboxylic acids to *trans*-$Ir(CO)Cl(P(C_6H_5)_3)_2$. These products would be expected to have the structure with the trans Cl–Ir–H geometry[10a] and thus have the carboxylato ligand trans to CO. The low stability of such complexes might be attributed to proton abstraction by the carboxylate anion which would be more readily labilized in a trans RCO_2–Ir–CO arrangement than in a trans RCO_2–Ir–Cl arrangement as in **3**.

Other nucleophiles such as pyridine, benzonitrile, *p*-toluisonitrile, and dimethylphenylphosphine were found to add to the bidentate carboxylato complexes **2** to form the monodentate carboxylato complexes **4–7** with structures analogous to **3**. Thus it is likely that the nucleophile adds in the same position previously indicated for the carbonyl. Pertinent spectral data are shown in Table III. The Ir–Cl stretching frequencies of these complexes (**4–7**) support our assignment of a structure with Cl trans to RCO_2 rather than trans to L or H. The addition of dimethylphenylphosphine gives a product with a nmr doublet at τ 8.02 ($J(P–CH_3)$ = 7.0 cps) which indicates that the added ligand is cis to two triphenylphosphine ligands and that the compound has a plane of symmetry through the methyl–phosphorus–iridium bond.[12]

Conclusions

It has previously been noted that weak carboxylic acids react reversibly with iridium(I)–carbonyl complexes and it has not been possible to isolate carboxylatohydridocarbonyliridium complexes.[6] The oxidative addition of carboxylic acids to the dinitrogen complex **1** proceeds with evolution of nitrogen and formation of hydrido bidentate carboxylato complexes which are readily isolable. Carbonylation of the bidentate carboxylato complexes yields hydrido(monodentate carboxylato)carbonyl complexes **3**. Nucleophilic addition to these complexes proceeds at a site trans to the hydrido ligand.

Experimental Section

Materials and Methods.—Reagent grade carboxylic acids were used without further purification. Deuterioacetic acid was kindly provided by Dr. P. C. Myhre. Benzene was distilled and stored over molecular sieves. The dinitrogen complex **1** was prepared according to previously described procedures.[13] All reactions of the dinitrogen complex **1** were conducted in a nitrogen atmosphere. Infrared spectra were obtained as Nujol or hexachlorobutadiene mulls using a Perkin-Elmer Model 621 grating spectrophotometer. A Varian A-60 spectrometer was used to obtain nmr data. Microanalyses were performed by Dr. F. Pascher, Bonn, Germany.

Chlorohydridocarboxylatobis(triphenylphosphine)iridium(II), 2.—Acetic acid (0.5 ml) was added to a suspension of 200 mg of the dinitrogen complex **1** in 4 ml of benzene. After the mixture was stirred for 48 hr, the pale yellow product was filtered and washed with anhydrous ether. The other hydridocarboxylato complexes **2** were prepared in a similar fashion. Nearly quantitative yields were obtained.

Chlorohydridocarboxylatobis(triphenylphosphine)carbonyliridium(III), 3.—When a suspension of 100 mg of the hydridocarboxylato complex **2** in 2 ml of benzene was treated with carbon monoxide (20 psi), a colorless solution was formed. Addition of *n*-hexane afforded a white solid which was filtered and washed with hexane. The products could be recrystallized from benzene–hexane.

The nucleophiles pyridine, benzonitrile, *p*-toluisonitrile, and dimethylphenylphosphine were added to suspensions of the hydridocarboxylato complexes **2** in benzene. These mixtures were stirred for 1 hr or longer, and *n*-hexane was added to decrease the solubilities of the products. These products were filtered and washed with hexane. The yields were 80–90%.

Acknowledgments.—We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. This research was also supported by the National Science Foundation through Grants GY 7269 and GY 6152.

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The Reaction of TCNQ (2,5-Cyclohexadiene-$\Delta^{1(\alpha),4(\alpha')}$-dimalononitrile) with a Cobalt(II) Schiff Base Complex

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Received July 15, 1971

The reaction of tetracyanoethylene (TCNE) with the Schiff base complex *N,N'*-ethylenebis(acetylacetoniminato)cobalt(II), [Co(acacen)], in the presence of pyridine was recently reported.[1] The products isolated were the 2:1 adducts [{Co(acacen)py}$_2$TCNE], which were obtained in two isomeric forms and shown to contain a nitrile-bonded TCNE moiety. This paper describes the reaction of 2,5-cyclohexadiene-$\Delta^{1(\alpha),4(\alpha')}$-dimalononitrile (TCNQ)

with [Co(acacen)] in the presence of pyridine. This system was investigated in order to determine any difference in behavior between TCNE and the more electronegative TCNQ. Differences in behavior of these two cyano compounds have previously been noted. For example, the TCNE$^-$ radical anion is normally bonded to the metal in complexes, either through the C=C bond[2] or through the nitrile nitrogens,[3] whereas TCNQ$^-$ is generally found as a free radical anion[4] or as dimers or clusters of TCNQ$^-$ and TCNQ.[5]

Experimental Section

Materials.—The reagents 2,4-pentanedione, ethylenediamine, and $CoCl_2 \cdot 6H_2O$ were obtained commercially and used without further purification. The TCNQ (Eastman Organic Chemicals) was sublimed (150°; 0.5 mm) before use.

Preparation of Complexes.—The preparation and manipulation of [Co(acacen)] were carried out in deoxygenated solvents under an atmosphere of prepurified nitrogen.

[Co(acacen)].—The Schiff base *N,N'*-ethylenebis(acetyl-

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