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%.

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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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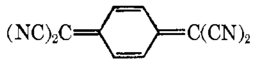
The reaction of tetracyanoethylene (TCNE) with the Schiff base complex *N,N'*-ethylenebis(acetylacetoniminato)cobalt(II), [Co(acacen)], in the presence of pyridine was recently reported.[1] The products isolated were the 2:1 adducts [{Co(acacen)py}$_2$TCNE], which were obtained in two isomeric forms 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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acetonimine) was prepared by the literature method.[6] The cobalt complex was prepared by a modification of the method of Everett and Holm.[7]

$[Co(acacen)(py)_2]TCNQ$.—A solution of $[Co(acacen)]$ (0.08 g, 0.29 mmol) and pyridine (0.5 ml) in deoxygenated toluene (10 ml) was slowly added to a solution of TCNQ (0.06 g, 0.29 mmol) in deoxygenated toluene (150 ml). The green solid which precipitated was collected, recrystallized from acetone–toluene, washed with toluene, and dried under vacuum; yield 0.15 g, 90%. *Anal.* Calcd for $[Co(acacen)(py)_2]TCNQ$: C, 63.46; H, 4.98; N, 17.42; Co, 9.16. Found: C, 63.3; H, 5.0; N, 17.2; Co, 9.0.

$[Co(acacen)(py)_2]PF_6$.—This complex was prepared from a saturated acetone solution of $[Co(acacen)(py)_2]TCNQ$ (0.2 g, 0.31 mmol) by addition of a saturated acetone solution of $NaPF_6$ (0.05 g, 0.31 mmol). Addition of toluene (4 times the volume of acetone) precipitated NaTCNQ which was removed by filtration. Extraction of the filtrate with water and evaporation of the aqueous extracts to a small volume yielded a brown solid. The solid was filtered, dissolved in acetone, reprecipitated with toluene, and dried under vacuum; yield 0.14 g, 90%. *Anal.* Calcd for $[Co(acacen)(py)_2]PF_6$: C, 45.21; H, 4.79; N, 9.59. Found: C, 45.2; H, 4.8; N, 9.2.

$[Co(acacen)(py)_2]BPh_4$.—This complex was prepared similarly. *Anal.* Calcd for $[Co(acacen)(py)_2]BPh_4$: C, 72.85; H, 6.33; N, 7.39. Found: C, 73.0; H, 6.7; N, 7.0.

$[Co(acacen)(py)_2]_2TCNQ$.—This complex was prepared by two methods.

Method 1.—A solution of $[Co(acacen)(py)_2]TCNQ$ (4.0 g, 7.0 mmol) in deoxygenated acetone (10 ml) was slowly added to a stirred solution of $[Co(acacen)]$ (2.0 g, 7.0 mmol) and pyridine (3 ml) in deoxygenated toluene (80 ml). After stirring for 0.5 hr, the brown precipitate was collected, washed with a 1% solution of $[Co(acacen)]$ in toluene and pyridine, and dried under vacuum. *Anal.* Calcd for $[Co(acacen)(py)_2]_2TCNQ$: C, 62.10; H, 5.54; N, 15.52; Co, 10.89. Found: C, 62.0; H, 5.8; N, 15.1; Co, 11.1.

Method 2.—A solution of TCNQ (0.06 g, 0.29 mmol) in deoxygenated toluene (150 ml) was added dropwise to a stirred solution of $[Co(acacen)]$ (0.18 g, 0.60 mmol) and pyridine (0.5 ml) in deoxygenated toluene (10 ml). After stirring for 0.5 hr, the brown precipitate was collected, washed with a 1% solution of $[Co(acacen)]$ in toluene and pyridine, and dried under vacuum. The physical (ir and uv spectra) and chemical (reaction with polar solvents) properties of this product indicated its identity with that prepared by method 1.

Analyses.—Elemental analyses for C, H, and N were performed by Miss H. Beck of this department. Cobalt was estimated by a spectrophotometric technique.[8]

Physical Measurements.—The ir spectra were recorded on a Perkin-Elmer 337 spectrophotometer and KBr disks and Nujol mulls were used for solids. Electronic spectra of solutions were recorded using matched 1-cm quartz cells on a Cary 14 spectrophotometer. Diffuse reflectance spectra of solids diluted in KBr were recorded on a Beckman DU spectrophotometer with a diffuse reflectance attachment and on a Cary 14 spectrophotometer with a Cary 1411 reflectance attachment. The epr measurements were made on a Varian Associates V-4500 spectrometer operating at the X-band frequency and calibrated against DPPH powder ($g = 2.0036$). Magnetic susceptibilities of solid samples were determined on a Faraday balance. Conductivities of 10^{-3} *M* solutions of complexes in nitromethane were measured on an Industrial Instruments Model RC 16B1 conductivity bridge.

Results and Discussion

The air-stable green solid obtained when $[Co(acacen)]$ and TCNQ are mixed in a 1:1 ratio in the presence of pyridine analyzes for $Co(acacen)(py)_2TCNQ$. The solid (Nujol mull) exhibits a strong absorption at 1600 cm^{-1}, characteristic of coordinated pyridine.[9] The compound is paramagnetic with one unpaired electron per mole ($\mu_{eff} = 1.71$ BM). The epr measurements of toluene solutions of the complex show the nine-line pattern ($g = 2.0029$, total width 15 G) expected[5] for $TCNQ^-$ (arising from coupling of the unpaired electron with four equivalent nitrogens with $I = 1$), and epr measurements of solid samples show a single narrow peak ($g = 2.0029$, width 15 G). If the unpaired electron were on the cobalt atom, a very different and much broader (1200 G) epr spectrum would be expected.[10] The electronic spectrum of acetone solutions of the complex shows the very characteristic spectrum[5] of $TCNQ^-$, and the same spectrum, but with much lower resolution, is observed in the diffuse reflectance spectrum.

Thus, this green complex consists of a six-coordinate cobalt(III) cation, $[Co(acacen)(py)_2]^+$, and the anion radical $TCNQ^-$, formed according to Scheme I. Additional evidence for this formulation was obtained by the isolation of the diamagnetic BPh_4^- and PF_6^- salts of this same cation $[Co(acacen)(py)_2]^+$ from solutions of the green complex. Electronic spectra of acetone and acetonitrile solutions of these salts agreed well with the published spectrum of the cation.[11]

SCHEME I

$$py + [Co^{II}(acacen)py] + TCNQ \xrightarrow{\text{toluene}} [Co^{III}(acacen)(py)_2]TCNQ$$

$$2py + 2[Co^{II}(acacen)py] + TCNQ \xrightarrow{\text{toluene}} [Co^{III}(acacen)(py)_2]_2TCNQ$$

$$py + [Co^{III}(acacen)(py)_2]TCNQ + [Co^{II}(acacen)py] \underset{\text{toluene}}{\overset{\text{polar solvents}}{\leftrightarrows}} [Co^{III}(acacen)(py)_2]_2TCNQ$$

The diamagnetic, air-stable brown solid prepared by reaction of $[Co(acacen)py]$ with $[Co(acacen)(py)_2]TCNQ$ in the presence of pyridine and directly from $[Co(acacen)py]$ and TCNQ in a 2:1 ratio in the presence of pyridine is formulated as $[Co(acacen)(py)_2]_2TCNQ$. The analyses are in good agreement with this formulation and the ir spectrum (Nujol mull) again showed the presence of coordinated pyridine. Attempts to recrystallize this complex showed that in all solvents in which it was soluble, $[Co^{III}(acacen)(py)_2]TCNQ$ and $[Co^{II}(acacen)py]$ were regenerated (from the electronic spectrum showing $TCNQ^-$ and the epr spectrum showing $[Co(acacen)py]$[10]) according to Scheme I.

The diamagnetism and the epr spectrum (which shows only an extremely weak signal of $TCNQ^-$ from trace impurities) show the absence of significant amounts of $TCNQ^-$ or Co(II) salts in the solid product. Similarly the diffuse reflectance spectrum shows the same two bands as found for $[Co(acacen)(py)_2]TCNQ$ at 770 and 870 nm but only $^1/_{1000}$th of the intensity (using the Kubelka–Munk remission function[12]) confirming the presence of only negligible amounts of

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$TCNQ^-$. In the region 300–600 nm, the brown solid shows strong bands at 345 and 492 nm (compared with 365 and 500 nm for the green $TCNQ^-$ salt).

Thus the brown product is formulated as the $[Co(acacen)(py)_2]^+$ salt of $TCNQ^{2-}$, rather than as a nitrile-bonded dimer similar to those of TCNE described earlier.[1] This compound is the first salt of the $TCNQ^{2-}$ anion to be reported. The $TCNQ^{2-}$ anion has only been previously known in solution from the electrochemical reduction of TCNQ.[13] As shown above, this anion is diamagnetic and does not show any electronic transitions in the visible region. The ir spectrum of the brown complex shows only two $C{\equiv}N$ stretches at 2151 and 2102 cm^{-1}, whereas Crumbliss and Basolo[1] found five such bands for the nitrile-bonded TCNE dimers. The lowering of the frequency of these two bands from those of $TCNQ^-$ (at 2171 and 2145 cm^{-1} in solid $[Co(acacen)(py)_2]TCNQ$; at 2177 and 2144 cm^{-1} in acetone solution) is consistent with the $TCNQ^{2-}$ formulation, where a further electron has been placed in the antibonding orbitals, thereby weakening the $C{\equiv}N$ bonds.

The behavior of TCNQ with [Co(acacen)py] in the presence of pyridine summarized in Scheme I contrasts markedly with that observed for TCNE.[1] The analogous $[Co(acacen)(py)_2]TCNE$ salt is not isolated from 1:1 mixtures of [Co(acacen)py] and TCNE in the presence of pyridine, but the nitrile-bonded dimers precipitate. However, these dimers in CH_2Cl_2 solution do give the $TCNE^-$ radical anion, a reaction analogous to that of the brown 2:1 adduct of TCNQ. The structures of the 2:1 adducts are very different in the TCNQ case (containing a second mole of coordinated pyridine and ionic $TCNQ^{2-}$) and the TCNE cases (the species contain $Co{-}N{\equiv}C{-}$ linkages). These differences in behavior can be rationalized by considering the different redox properties of the two compounds TCNQ and TCNE (see Table I).

Table I

Reduction Potentials ($E_{1/2}$, V) *vs.* Standard Calomel Electrode

$TCNQ^a$	$TCNE^a$	$[Co^{III}(acacen)(py)_2]^{+\,b}$
+0.10	+0.14	−0.47
−0.39	−0.75	

[a] Solvent CH_3CN, with 0.1 *M* Et_4NClO_4 as supporting electrolyte. [b] From ref 14.

From the reduction potential for $[Co^{III}(acacen)(py)_2]^+$, it is clear that the production of $TCNQ^{2-}$ in the third step of Scheme I would have an equilibrium constant of ~0.5 in 1 *M* solutions and could be driven to the right by the insolubility of the product (and reversed on solution of the product). A similar reaction forming the analogous $TCNE^{2-}$ salt would have an equilibrium constant of 10^{-7} and hence does not occur, the product obtained containing the $Co{-}N{\equiv}C{-}$ linkages rather than the free dianion.

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The Slow Isomerization of 2-[Trifluoromethyl(trifluoromethylthio)-phosphino]pentaborane. Other New Phosphinopentaboranes[1]

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Compounds of the type $2,3\text{-}\mu\text{-}R_3MB_5H_8$ (M = Si, Ge, Sn, Pb) have been reported to isomerize slowly (usually by heating) to $2\text{-}R_3MB_5H_8$,[2] convertible with even more difficulty to $1\text{-}R_3MB_5H_8$.[3] However, the known phosphinopentaboranes have either persisted as $2,3\text{-}\mu\text{-}R_2PB_5H_8$ or appeared only as $1\text{-}R_2PB_5H_8$.[4]

We now have made some new phosphinopentaboranes, one of which was isolated first as $2\text{-}(CF_3SPCF_3)B_5H_8$, slowly convertible at 25° to $1\text{-}(CF_3SPCF_3)B_5H_8$. The others involved more strongly basic phosphine groups, which remained in the 2,3-bridge position.

This study required the synthesis of the new compound $(CF_3S)_2PCF_3$, which was made quantitatively by the cleavage of $(CF_3P)_4$ by $(CF_3S)_2$ at 200°. This process, as well as the new quantitative synthesis of the known compound $CF_3SP(CF_3)_2$ from $P_2(CF_3)_4$ and $(CF_3S)_2$, might be regarded as analogous to the nucleophilic action of $CH_3S{-}SCH_3$ on the P–P bond[5] or perhaps more appropriately as a pseudohalogen action by $CF_3S{-}SCF_3$, like the long known cleavage of $(CF_3P)_4$ or $P_2(CF_3)_4$ by iodine. Both trifluoromethylthiophosphines seemed to have excellent stability, having been formed without loss at 200°. The reported instability of $CF_3SP(CF_3)_2$[6] presumably was an effect of catalytic impurities, not excluded by the original method of synthesis.

The New Thiophosphine.—A sample of $(CF_3P)_4$[7] (purified by recrystallization from hexane in the absence of air) was exposed to a fivefold proportion of $(CF_3S)_2$ in a sealed Pyrex tube at 200°. The reaction progressed only moderately during 1 day but was complete after 3 days. The millimolar stoichiometry of a typical run is shown as follows.

$$\begin{array}{cccc} (CF_3P)_4 & +\ 4(CF_3S)_2 & \longrightarrow & 4(CF_3S)_2PCF_3 \\ 1.78 & 8.5 & & 7.1 \\ & \underline{-1.4} & & \\ & 7.1 & & \end{array}$$

The product was isolated by high-vacuum fractional condensation, using U traps at −23, −78, and −196°. No $(CF_3P)_4$ or $(CF_3P)_5$ was found in the −23° trap. For isolation and measurement of the unused $(CF_3S)_2$, the last of it was removed from the product by a small reflux column at −78°.

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