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METAL COMPLEXES OF CYANOCARBONS
IX*. DICYANOACETYLENE COMPLEXES OF SOME NOBLE METALS

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SUMMARY

Reactions of dicyanoacetylene with a number of iridium, rhodium, nickel, palladium, and gold substrates have been studied under preparative conditions and several new complexes have been isolated and characterized. These include, for iridium, $IrX(CO)(C_4N_2)(EPh_3)_2$ ($E=As$, $X=Cl$; $E=P$, $X=Cl$, Br, I, NCS), and a σ-dicyanovinyl π-dicyanoacetylene complex $Ir[C(CN)=CHCN](CO)(C_4N_2)(PPh_3)_2$, for rhodium, $RhCl(CO)(C_4N_2)(PPh_3)_2$, and for palladium, $Pd(C_4N_2)(PPh_3)_2$. Comparisons of dicyanoacetylene as a ligand are made with other cyanocarbons and with other activated acetylenes.

INTRODUCTION

In our investigations of transitional metal complexes of cyanocarbons, we previously described some very stable compounds derived from reactions of the strong π-acid dicyanoacetylene with electron-rich platinum substrates, *e.g.* $Pt(PPh_3)_4$. For further clarification of the coordination chemistry of dicyanoacetylene, reactions of it with various d^8 and d^{10} complexes of nickel, palladium, rhodium, iridium, and gold have been carried out. Side-reactions resulting in the formation of intractable materials precluded the isolation of compounds from many of the reactions, but a number of new iridium complexes and a few rhodium and palladium compounds were obtained and are described herein. Following our brief report[2] of some of this work, the independent preparation of several dicyanoacetylene complexes was described[3].

EXPERIMENTAL

I. Materials

Dicyanoacetylene was prepared by a minor modification of the method of Moureu and Bongrand[4].

Literature methods were used to prepare the noble metal substrates which were used as starting materials. Thus prepared were the following: $IrX(CO)(PPh_3)_2$

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* For part VIII see ref. 1.

($X = Cl^5$, Br, I, NCS)*, $IrCl(CO)(AsPh_3)_2$**, $IrCl(N_2)(PPh_3)_2$[7], $[Ir(Diphos)_2(CO)]Cl_8$, $[Ir(Diphos)_2]Cl$[8] (Diphos $= Ph_2PCH_2CH_2PPh_2$), $IrH(CO)(PPh_3)_3$[9], $IrH(CO)_2(PPh_3)_2$[10], $IrH(CO)(C_4H_2N_2)(PPh_3)_2$[11], $[RhCl(CO)_2]_2$[12], $RhCl(CO)(PPh_3)_2$[13], $RhCl(CO)_2(PPh_3)$[14], $[RhCl(PPh_3)_2]_2$[15], $RhCl(PPh_3)_3$[15]. $PdCl_2(PhCN)_2$[16], $Pd(PPh_3)_4$[17], $(Et_4N)_2[Pd_2Br_6]$[18], $Ni(PPh_3)_2(C_2H_4)$[17], and $AuCl(PPh_3)_2$[19]. The complex $Ni(CO)_2$(Diphos) was a commercial product and was recrystallized from ethanol before use.

Thiophene-free benzene was dried over sodium wire. Tetrahydrofuran was refluxed over sodium, treated with $LiAlH_4$ and distilled, and stored over molecular sieves. All other chemicals used were reagent-grade materials, and were used without further purification.

Due to the sensitivity of C_4N_2 to oxygen, all reactions were carried out in a nitrogen atmosphere, but work-up of reaction mixtures was usually done in the open atmosphere. Dicyanoacetylene was stored at −78° under nitrogen. For carrying out a reaction, the C_4N_2 was allowed to warm to room temperature where it liquified, and subsequently it was syringed into the reaction vessel.

II. Preparation of some dicyanoacetylene complexes of iridium

A. Chlorocarbonyl(dicyanoacetylene)bis(triphenylphosphine)irridium, $IrCl(CO)(C_4N_2)(PPh_3)_2$. Vaska's compound, $IrCl(CO)(PPh_3)_2$ (0.78 g, 1 mmole) was dissolved in 100 ml of dry, deoxygenated benzene, dicyanoacetylene (0.16 ml, 2 mmoles) was added to the magnetically-stirred solution at room temperature and immediately the bright-yellow solution of Vaska's compound changed color to pale red-orange. After $\frac{1}{2}$ h of stirring the solvent was removed under reduced pressure to give a red-brown residue which was recrystallized from benzene/methanol as 0.84 g (98%) of peach-colored crystals; m.p. 200–250 (dec.); IR*** (mull) 1728 m ($C\equiv C$), 1988 w ($C\equiv O$) 2025 vs ($C\equiv O$), and 2192 m ($C\equiv N$); IR (CH_2Cl_2) 1710 m ($C\equiv C$), 1730 m ($C\equiv C$), 2018 vs, sp ($C\equiv O$), and 2195 m ($C\equiv N$). An analytical sample was obtained by recrystallization from dichloromethane/hexane. (Found: C, 57.98; H, 3.73; Cl, 4.36; N, 3.51; mol.wt. in benzene, 845. $C_{41}H_{30}ClIrN_2OP_2$ calcd.: C, 57.49; H, 3.53; Cl, 4.15; N, 3.27%; mol.wt., 856.)

B. Bromocarbonyl(dicyanoacetylene)bis(triphenylphosphine)irridium, $IrBr(CO)(C_4N_2)(PPh_3)_2$. The complex $IrBr(CO)(PPh_3)_2$ (0.41 g, 0.5 mmoles) and C_4N_2 (0.15 ml, 2 mmoles) reacted immediately in benzene (100 ml) at room temperature to give a pale pink solution. After 10 min of stirring the solvent was removed to give 0.4 g of pink residue which was washed well with methanol and recrystallized from benzene/methanol to give orange needles; m.p. 188–190 (dec.); IR (mull) 1795 m ($C\equiv C$), 1996 s ($C\equiv O$), 2023 vs ($C\equiv O$), and 2190 m ($C\equiv N$). (Found: C, 54.88; H, 3.59; N, 3.12; mol.wt. in benzene, 875. $C_{41}H_{30}BrIrN_2OP_2$ calcd.: C, 54.67; H, 3.36; N, 3.11%; mol.wt., 905.)

C. Iodocarbonyl(dicyanoacetylene)bis(triphenylphosphine)iridium, $IrI(CO)$-

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* The related compounds for X = Br, I, and NCS were obtained from $IrCl(CO)(PPh_3)_2$ by metathesis.

** Prepared from $Na_3IrCl_6 \cdot 12H_2O$ by a procedure analogous to that used for $IrCl(CO)(PPh_3)_2$[6].

*** Abbreviations used to describe infrared band intensities and widths are: s, strong; vs, very strong; m, medium; w, weak; sp, sharp; br, broad. For a shoulder the abbreviation is sh. All band positions are given in cm^{-1}. Mull spectra were recorded in either Nujol or hexachlorobutadiene.

$(C_4N_2)(PPh_3)$. Mixing $IRI(CO)(PPh_3)_2$ (0.95 g, 1 mmole) and C_4N_2 (0.20 ml, 2.5 mmoles) in 100 ml benzene at room temperature gave quickly a dark orange solution which was stirred for 10 min. The volume of the solution was reduced, and a solid separated. The red-brown shiny prisms were collected on a filter and became yellow and opaque. Recrystallization from dichloromethane/ethanol gave the complex; m.p. 187–189 (dec.); IR (mull) 1727 m ($C\equiv C$), 1979 m ($C\equiv O$), 2019 vs, sp ($C\equiv O$), and 2191 s, sp ($C\equiv N$). (Found: C, 52.46; H, 3.82; N, 2.87; mol.wt. in benzene, 953. $C_{41}H_{30}IIrN_2OP_2$ calcd.: C, 51.96; H, 3.19; N, 2.96%; mol.wt., 948.)

D. (Isothiocyanato)carbonyl(dicyanoacetylene)bis(triphenylphosphine)irridium, $Ir(NCS)(CO)(C_4N_2)(PPh_3)_2$. A reaction mixture containing $Ir(NCS)(CO)(PPh_3)_2$ (0.6 g, 0.75 mmoles) and dicyanoacetylene (0.12 ml, 1.5 mmoles) in 20 ml of CH_2Cl_2 was stirred at room temperature for 10 min. To the pale-red mixture was added ethanol, and as the volume was reduced pink crystals, 0.59 g (90%), precipitated; m.p. 138–144 (dec.); IR (mull) 844 w (C=S), 1705 m ($C\equiv C$), 2036 vs ($C\equiv O$), 2089 vs ($C\equiv N$ of NCS), and 2192 m ($C\equiv N$ of C_4N_2). (Found: C, 56.94; H, 3.26; N, 4.69; mol.wt. in $CHCl_3$, 795. $C_{42}H_{30}IrN_3OP_2S$ calcd.: C, 57.39; H, 3.44; N, 4.78%; mol.wt., 879.)

E. Chlorocarbonyl(dicyanoacetylene)bis(triphenylarsine)iridium, $Ir(CO)(C_4N_2)(AsPh_3)_2$. The compound $IrCl(CO)(AsPh_3)_2$ (0.5 g, 0.5 mmole) was dissolved in benzene (20 ml) and C_4N_2 (0.12 ml, 1.5 mmoles) was added at room temperature to give a pale-orange solution. The reaction mixture was taken to dryness under reduced pressure, the residue was washed well with methanol, and recrystallized from dichloromethane/heptane as dark orange crystals, 0.4 g (70%); m.p. 172–174 (dec.); IR (mull) 1710 m ($C\equiv C$), 1720 m ($C\equiv C$), 2002 vs ($C\equiv O$), and 2190 m ($C\equiv N$). (Found: C, 51.05; H, 3.12; N, 2.99. $C_{41}H_{30}AsClIrN_2O$ calcd.: C, 52.16; H, 3.20; N, 2.97%.)

F. *(Dicyanovinyl)carbonyl(dicyanoacetylene)bis(triphenylphosphine)iridium, $Ir[C(CN)=CHCN](CO)(C_4N_2)(PPh_3)_2$*. The addition of C_4N_2 (0.10 ml, 1.2 mmoles) to a solution of $IrH(CO)_2(PPh_3)_2$ (0.39 g, 0.5 mmoles) in 75 ml of 2/1 benzene/CH_2Cl_2 at room temperature caused an immediate darkening of the mixture to give an intense greenish-black solution. After 5 min of stirring, 50 ml of ethanol was added and the volume of the solution was reduced. A solid precipitated, and this was collected and twice recrystallized from dichloromethane/ethanol to give pale-pink crystals; m.p. 200–210 (dec.); IR (mull) 1545 w (C=C), 1698 m ($C\equiv C$), 2021 vs, sp ($C\equiv O$), 2177 sh ($C\equiv N$), 2188 s, sp ($C\equiv N$), and 2210 sh ($C\equiv N$). (Found: C, 60.09; H, 3.34; N, 6.21. $C_{45}H_{31}IrN_4OP_2$ calcd.: C, 60.19; H, 3.48; N, 6.24%.)

III. Preparation of a dicyanoacetylene complex of rhodium

Chlorocarbonyl(dicyanoacetylene)bis(triphenylphosphine)rhodium, $RhCl(CO)(C_4N_2)(PPh_3)_2$. The rhodium complex $RhCl(CO)(PPh_3)_2$ (0.77 g, 1 mmole) in 50 ml of CH_2Cl_2 was treated at room temperature with C_4N_2 (0.32 ml, 4 mmoles), and an orange solution was obtained immediately. Addition of hexane (50 ml) caused brown crystals to separate, 0.62 g (80%); m.p. 199–203 (dec.); IR (mull) 1775 m ($C\equiv C$), 2017 w ($C\equiv O$), 2046 vs, sp ($C\equiv O$), and 2192 s, sp ($C\equiv N$). (Found: C, 63.57; H, 4.12; N, 3.59. $C_{41}H_{30}ClIrN_2OP_2$ calcd.: C, 64.20; H, 3.95; N, 3.65%.)

IV. Preparation of a dicyanoacetylene complex of palladium

Fumaronitrile (2.5 g, 33.4 mmoles) was added to $Pd(PPh_3)_4$ (5.5 g, 5 mmoles) in 100 ml of benzene at room temperature and a clear, pale-pink solution was obtained.

Concentration of the solution to 50 ml, followed by addition of 50 ml of ethanol caused white crystals of *fumaronitrilebis(triphenylphosphine)palladium*, $Pd(C_4N_2H_2)$, 2.5 g (70%) to separate; m.p. 141–154 (dec.); IR (mull) 2206 s (C≡N). (Found: C, 67.40; H, 4.30; N, 3.67; mol.wt. in benzene 700. Calcd.: C, 67.76; H, 4.55; N, 3.94%; mol.wt., 709.) The complex is partially soluble in ethanol and quite soluble in acetone, dichloromethane, and chloroform.

The complex $Pd(C_4N_2H_2)(PPh_3)_2$ (5.6 g, 8 mmoles) was dissolved in 100 ml of benzene, treated at 10° with C_4N_2 (0.96 ml, 12 mmoles), and gave after a few minutes a clear red solution. Solvent was removed after 10 min and the dark solid so obtained was washed well with methanol. It was twice recrystallized from dichloromethane/methanol to give 1.7 g (32%) of orange crystals; m.p. 157–160 (dec.); IR (mull) 1751 m (C≡C) and 2187 s (C≡N). (Found: C, 67.34; H, 4.01; N, 3.89; mol.wt. in $CHCl_3$ 718. $C_{40}H_{30}N_2P_2Pd$ calcd.: C, 67.95; H, 4.29; N, 3.96%; mol.wt., 707.)

Attempts to prepare $Pd(C_4N_2)(PPh_3)_2$ from $Pd(PPh_3)_4$ gave a red tar from which no well characterized complex could be obtained.

V. Analyses and instrumentation

Analyses for carbon, hydrogen, and nitrogen were carried out by Mr. R. Seab of the Department of Chemistry, Louisiana State University. Other analyses were performed by Galbraith Laboratories, Inc., of Knoxville, Tennessee.

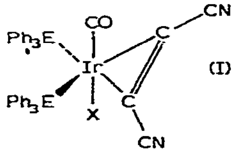
Infrared spectra in the NaCl region were measured with a Beckman IR-7 spectrophotometer in Nujol or hexachlorobutadiene mulls, KBr pellets, and dichloromethane solutions.

Molecular weights were measured using a Hewlett–Packard osmometer, Model 302A, with a 37° probe. Chloroform or benzene was used as a solvent.

RESULTS AND DISCUSSION

A. Iridium

Dicyanoacetylene reacted immediately at ambient temperatures with the iridium(I) substrates $IrX(CO)(EPh_3)_2$ (E = As, X = Cl; E = P, X = Cl, Br, I, NCS) in benzene solution to give the complexes $IrX(CO)(C_4N_2)(EPh_3)_2$. These complexes are pink to pale-orange in color and appear to be stable indefinitely in the solid state. Solutions of the complexes deteriorate in a few days, particularly for the isothiocyanato complex. Thermal stabilities are good with decomposition occurring in the 175–200° range, but these stabilities are not as good as for the analogous tetracyanoethylene complexes which decompose in the 200–300° range[20]. The similarity of the complexes' infrared spectral patterns to those of related complexes of fumaronitrile and tetracyanoethylene whose structures are known[21,22] suggest structure (I) for $IrX(CO)(C_4N_2)(EPh_3)_2$.



(I)

TABLE 1

CARBONYL STRETCHING FREQUENCIES IN COMPLEXES OF THE TYPE $IrCl(CO)L(PPh_3)_2$

L	$\nu(C{\equiv}O)$ (cm^{-1})	Phase	Ref.
No ligand	1967	$CHCl_3$	22
$MeOOC{-}C{\equiv}C{-}COOMe$	1980	KBr	35
$HOOC{-}C{\equiv}C{-}COOH$	2005	KBr	35
O_2	2015	$CHCl_3$	22
$NC{-}C{\equiv}C{-}CN$	2018	CH_2Cl_2	This work
SO_2	2021	Nujol	22
$CF_3{-}C{\equiv}C{-}CF_3$	2025	$CHCl_3$	22
$NCCH{=}CHCN$	2029	CH_2Cl_2	20
$F_2C{=}CF_2$	2052	$CHCl_3$	22
$(NC)_2C{=}C(CN)_2$	2060	CH_2Cl_2	20
BF_3	2067	C_6D_6	36

Comparisons of the carbonyl stretching frequencies in the infrared spectra of $IrX(CO)(C_4N_2)(PPh_3)_2$ with $\nu(C{\equiv}O)$ values of complexes formed from the reactions of Vaska-type compounds with π-acids and/or electrophiles serve to delineate the characteristics of dicyanoacetylene as a ligand. It is generally believed that $\nu(C{\equiv}O)$ values in complexes of the type $IrCl(CO)(ligand)(PPh_3)_2$ which are greater than 1967 cm^{-1} [*i.e.*, $\nu(C{\equiv}O)$ of the parent $IrCl(CO)(PPh_3)_2$ substrate] can be correlated with the degree to which electron density has been removed from the iridium atom by "ligand"[23]. One sees from Table 1 that dicyanoacetylene is comparable to oxygen and sulfur dioxide in its Lewis acid capacity here. One also notes that the simplest olefinic cyanocarbon, tetracyanoethylene, is a much better agent for removal of electron density from the iridium atom than is the simplest acetylenic cyanocarbon, dicyanoacetylene. Shown in Table 2 are data for tetracyanoethylene, *trans*-1,2-dicyanoethylene (fumaronitrile), and dicyanoacetylene complexes of iridium, and it is seen that the latter two are quite comparable in their ability to alter the electronic environment at the central atom in these complexes.

When dicyanoacetylene was added to a benzene solution of the hydrido-iridium(I) complex $IrH(CO)(PPh_3)_3$ at ambient temperature a dark-red solution was obtained immediately and all attempts to work-up the mixture gave only intractable

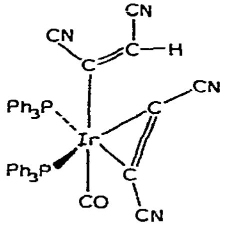
TABLE 2

CARBONYL STRETCHING FREQUENCIES IN COMPLEXES OF THE TYPE $IrX(CO)L(PPh_3)_2$[a,b]

X	L		
	$(NC)_2C{=}C(CN)_2$	$NCCH{=}CHCN$	$NCC{\equiv}CCN$
Cl	2060	2029	2018
Br	2056	2030	2023[c]
I	2060[c]		2019[c]
NCS	2067	2043[d]	2036[c]

[a] Taken from ref. 20 and this work. [b] In CH_2Cl_2 solution unless noted otherwise. [c] Mull spectrum. [d] Unpublished observation.

tars. Since solutions of $IrH(CO)(PPh_3)_3$ probably contain some free triphenylphosphine from dissociation, it is presumed that the impediment to complex isolation in this reaction and others in this work (*vide infra*), as also in our previous study of platinum complexes[1], arises from formation of various diphosphoranes[24] perhaps accompanied by polymerization of dicyanoacetylene[25]. These problems were less pronounced in the reaction of C_4N_2 with the dicarbonyl $IrH(CO)_2(PPh_3)_2$, and pink crystals of a compound were obtained which contain the elements of two molecules of dicyanoacetylene per iridium atom. The compound is formulated as σ-(dicyanovinyl)carbonyl(π-dicyanoacetylene)bis(triphenylphosphine)iridium on the basis of elemental analysis and infrared spectral data [$\nu(C{\equiv}N)$ 2215 m, 2188 s, 2177 m; $\nu(C{\equiv}O)$ 2021 vs; $\nu(C{\equiv}C)$ 1698 m; and $\nu(C{=}C)$ 1545 w], and structure (II) is suggested



(II)

by analogy with what is known to be the structure of the compound obtained by reaction of tetracyanoethylene with the same iridium substrate[26]. Formation of (II) could occur sequentially via initial formation of a hydrido-π-dicyanoacetylene complex. Bonding of the good π-acid C_4N_2 to iridium must activate the Ir–H bond, and subsequent 1,2-addition to give a tetra-coordinate dicyanovinyl complex followed by reaction of this coordinatively unsaturated complex with another molecule of C_4N_2 would give (II). In the case of the reaction of $IrH(CO)_2(PPh_3)_2$ with tetracyanoethylene, a novel 1,4-addition occurs to give a keteniminato complex. With the dicyanoacetylene reaction, however, there is no strong infrared band at ca. 2130 cm^{-1} in the product suggestive of a M–N=C=C linkage, and we therefore propose 1,2-addition and a structure as (II). This compound is only the third example of a σ-vinyl π-acetylene transition metal complex. Previously such compounds were reported for the reactions of hexafluorobutyne and bis(methoxycarbonyl)acetylene with $IrH(CO)(PPh_3)_3$[11], and these are compounds which may be considered as models for intermediates in the linear polymerization of acetylenes as catalyzed homogeneously by transition metal substrates.

In view of the comparable Lewis acidic properties of fumaronitrile and dicyanoacetylene, as deduced above from $\nu(C{\equiv}O)$ values in $IrX(CO)$(cyanocarbon)$(PPh_3)_2$ complexes, it is of interest to note that fumaronitrile is not nearly so able to activate the Ir–H bond as in dicyanoacetylene. That is to say, the complex $IrH(CO)(C_4N_2H_2)(PPh_3)_2$ is a very stable compound and is not decomposed even after refluxing in toluene for 1 h[27], whereas in the reaction of $IrH(CO)_2(PPh_3)_2$ with C_4N_2, where as described above the compound $IrH(CO)(C_4N_2)(PPh_3)_2$ is believed to be formed initially as an intermediate, cleavage of the Ir–H bond occurs at room temperature, and the intermediate $IrH(CO)(C_4N_2)(PPh_3)_2$ could not be isolated. (As a matter of fact, a hydrido π-acetylene complex of a transition metal has never been reported.) The reason for this difference of fumaronitrile and dicyanoacetylene in their propensity to activate the Ir–H bond is not clear, but the difference may be general for olefins and acetylenes.

Reaction of dicyanoacetylene with the dinitrogen complex $IrCl(N_2)(PPh_3)_2$ gave a pink solid that was recrystallized from dichloromethane/methanol with some accompanying decomposition and/or transformation. The absence of a strong band around 2100 cm^{-1} in the infrared spectrum suggests that a nitrogen molecule is no longer coordinated to the iridium, and the elemental analysis indicates that two molecules of C_4N_2 are present per iridium atom. A formulation will not be offered until the reaction is studied more thoroughly.

The greater reactivity of the complex cation $[Ir(Diphos)_2]^+$ toward electrophilic reagents such as O_2, SO_2, etc., as compared to $IrCl(CO)(PPh_3)_2$[28], suggested to us that this Lewis base might react with various activated olefins and acetylenes as $IrCl(CO)(PPh_3)_2$ is well known to do. When either orange $[Ir(Diphos)_2]^+$ or white $[Ir(CO)(Diphos)_2]^+$ was treated with dicyanoacetylene only dark tars resulted. Particularly surprising was the fact that fumaronitrile, hexafluorobutyne, and phenylacetylene failed to react with $[Ir(Diphos)_2]^+$. So, while this substrate may be more reactive toward some reagents than is $IrCl(CO)(PPh_3)_2$, it appears that a reverse pattern exists for olefins and acetylenes.

B. Rhodium

Reactions of the rhodium complexes $RhCl(PPh_3)_3$, $[RhCl(PPh_3)_2]_2$, $RhCl(CO)(PPh_3)_2$, $RhCl(CO)_2PPh_3$ and $[RhCl(CO)_2]_2$ were studied, but in most cases well-characterized metal complexes could not be isolated. In retrospect this lack of success is understandable in view of the great reactivity of dicyanoacetylene and the propensity of rhodium(I) to promote catalytic processes. With $RhCl(PPh_3)_3$, the complicating features were aggravated by side reactions of C_4N_2 with triphenylphosphine where only a dark tar was obtained. In hopes of reducing the amount of tars that were forming the dinuclear complex, $[RhCl(PPh_3)_2]_2$, was allowed to react with C_4N_2 but here also dark-colored materials were formed. It was possible to isolate $RhCl(CO)(C_4N_2)(PPh_3)_2$ from the reaction of the rhodium analog of Vaska's compound with C_4N_2, but the complex was considerably less stable in solution than the iridium analog, and was more difficult to isolate and purify due to reversible dissociation of dicyanoacetylene. The dicarbonyl $RhCl(CO)_2PPh_3$ and the dinuclear complex $[RhCl(CO)_2]_2$ were allowed to react with C_4N_2 and brick-red and orange-red solids respectively were obtained. Their formulations are presently in doubt, but are being studied further.

C. Palladium

Unlike the reaction of $Pt(PPh_3)_4$ with C_4N_2 where the complex $Pt(C_4N_2)(PPh_3)_2$ was formed, for the analogous palladium case the gummy adducts of Ph_3P and C_4N_2 precluded isolation of the desired product. Monitoring of the reaction via infrared spectroscopy showed that $Pd(C_4N_2)(PPh_3)_2$ was formed, but it could not be isolated from the reaction mixture. Fortunately, C_4N_2 was found to cleanly displace fumaronitrile from $Pd(C_4N_2H_2)(PPh_3)_2$ to give orange needles of $Pd(C_4N_2)(PPh_3)_2$ in 80% yield. Reactions of dicyanoacetylene with the palladium substrates $PdCl_2(NCPh)_2$ and $(Et_4N)_2[Pd_2Br_6]$ did not lead to the isolation of well-characterized products although complexes were probably formed.

D. Nickel and gold

A dicyanoacetylene complex of nickel eluded our several attempts. The two substrated principally investigated were $Ni(CO)_2(Diphos)$ and $Ni(C_2H_4)(PPh_3)_2$. With the former intractable tars were gotten; with the latter a very exothermic reaction occurred, always with the production of black mixtures indicative of polymerization. In view of the relative stabilities of metal complexes of dicyanoacetylene as compared with other activated acetylenes (*vide infra*), and since several nickel–acetylene complexes have been reported[17], we believe that our negative results are due to improper experimental procedure rather than to inherent instability of the nickel–dicyanoacetylene bond.

No color change occurred when white $AuCl(PPh_3)$ was treated with dicyanoacetylene in benzene at room temperature. Upon refluxing the mixture for 45 min a yellow color developed but work-up gave only pure $AuCl(PPh_3)$. The reluctance of gold(I) to undergo the oxidative addition type reactions was further shown by the failure of $AuCl(PPh_3)$ to react with the very strong π-acid tetracyanoethylene.

E. Comments on the relative stabilities of some metal–acetylene complexes.

It is generally held that acetylenes substituted by electron-withdrawing functional groups form the most stable complexes with noble metals. These ideas of stabilities are not thermodynamically based, but have been inferred from (*a*) qualitative observations[29] of displacement reactions of the type depicted by eqn. (1):

$$Pt(PPh_3)_2(RC{\equiv}CR) + R'C{\equiv}CR' \rightleftharpoons Pt(PPh_3)_2(R'C{\equiv}CR') + RC{\equiv}CR \qquad (1)$$

(*b*) rate and equilibrium studies of the same type reactions[30,31] and (*c*) values[17] of $\Delta\nu(C{\equiv}C)$, *i.e.* the difference between the carbon–carbon stretching frequency of the free acetylene and the coordinated acetylene.

Shown in Table 3 are comparative data for dicyanoacetylene and hexafluorobutyne complexes. Insofar as thermal stabilities go, it is seen that the dicyanoacetylene complexes of platinum and iridium decompose at higher temperatures than do the C_4F_6 analogs but for palladium the reverse is true. Also shown in Table 3 are values of $\Delta\nu(C{\equiv}C)$, and it has been advocated that such data are, in fact, measurements of

TABLE 3

THERMAL DECOMPOSITION AND INFRARED DATA FOR ANALOGOUS HEXAFLUOROBUTYNE AND DICYANOACETYLENE COMPLEXES

Complex	M.p. (dec.) (°C)	$\nu(C{\equiv}C)$	$\Delta\nu(C{\equiv}C)$
$Pt(PPh_3)_2(C_4F_6)$	212–214	1763	525
$Pt(PPh)_2(C_4N_2)$	233–235	1683	436
$Pd(PPh_3)_2(C_4F_6)$	184–195	1838, 1811	475
$Pd(PPh_3)_2(C_4N_2)$	160–165	1751	368
$RhCl(CO)(C_4F_6)(PPh_3)_2$[a]			
$RhCl(CO)(C_4N_2)(PPh_3)_2$	199–203	1775	344
$IrCl(CO)(C_4F_6)(PPh_3)_2$	[b]	1770	530
$IrCl(CO)(C_4N_2)(PPh_3)_2$	200–250	1725	394

[a] Not reported. [b] The complex evolves C_4F_6 reversibly in the solid state. At 85° there is no gas evolution but at 110° all the hexafluorobutyne which was initially present in the complex is lost[37].

the thermodynamic stability of the complex. That is, the larger $\Delta\nu(C\equiv C)$ values are supposed to reflect a stronger attachement of the acetylene to the metal[17]. According to this criterion the C_4F_6 complexes of palladium, platinum, and iridium are more stable thermodynamically than are the analogous dicyanoacetylene complexes.

Shown in Table 4 are data which allow a comparison of some activated acetylenic complexes of platinum. Using the $\Delta\nu(C\equiv C)$ criterion, the platinum–acetylenic bond strength decreases in the order of the acetylene as follows:

TABLE 4

THERMAL DECOMPOSITION AND INFRARED DATA FOR PLATINUM COMPLEXES OF THE TYPE $Pt(PPh_3)_2(R{-}C\equiv C{-}R)$

L^a	M.p. (dec.) (°C)	$\nu(C\equiv C)$ (cm^{-1})	$\Delta\nu(C\equiv C)$
$NCC\equiv CCN^b$	233–235	1683	436
$CF_3C\equiv CCF_3^c$	212–214	1763	525
$MeOOCC\equiv CCOOMe^c$	188–190	1788	362^d
$PhC\equiv CH^e$	141–148	1687	428

[a] L = activated acetylene. [b] This work. [c] Ref. 17. [d] The value of $\nu(C\equiv C)$ for the uncoordinated acetylene was taken from a recent review[38]. [e] Ref. 39.

$$CF_3{-}C\equiv C{-}CF_3 > NC{-}C\equiv C{-}CN \sim Ph{-}C\equiv C{-}H > MeOOC{-}C\equiv C{-}COOMe \qquad (2)$$

Some doubt about the correctness of this ordering and the validity of the $\Delta\nu(C\equiv C)$ criterion arises when one considers the chemical reactivity of some of the acetylenic complexes. Kinetic studies[30,31] of displacement reactions [eqn. (1)] and related kinetic investigations[32,33] have been interpreted in terms of a dissociative mechanism, eqns. (3) and (4). Generally there is no correlation between thermodynamic stability and kinetic reactivity, but in the case of these reactions, as others have pointed out[30,31], the rate of the reaction as given by k_1 is a measure of the ease of rupture of the metal–acetylene bond. Even though $\Delta\nu(C\equiv C)$ values indicate that the platinum–dicyanoacetylene and platinum–phenylacetylene bond strengths are comparable, the solution behavior of these complexes suggests otherwise. Tetracyanoethylene displaces phenylacetylene (presumably via a dissociative mechanism as for acetylenic displacements) immediately at ambient condition from $Pt(PPh_3)_2(PhC\equiv CH)$[35] whereas dicyanoacetylene is displaced from $Pt(PPh_3)_2(C_4N_2)$ by a ten-fold excess of tetracyanoethylene only after 6–24 hours. Additionally, in view of the dissociative mechanism mentioned above, it seems reasonable that decomposition of the complexes in solution may proceed via dissociation of the acetylene [eqn. (5)] to generate $Pt(PPh_3)_2$,

$$Pt(PPh_3)_2(RC\equiv CR) \underset{k_{-1}}{\overset{\text{slow}\atop k_1}{\rightleftharpoons}} Pt(PPh_3)_2 + RC\equiv CR \qquad (3)$$

$$Pt(PPh_3)_2 + R'C\equiv CR' \xrightarrow{\text{fast}} Pt(PPh_3)_2(R'C\equiv CR') \qquad (4)$$

$$Pt(PPh_3)_2(RC\equiv CR) \rightleftharpoons Pt(PPh_3)_2 + RC\equiv CR \qquad (5)$$

a compound which is known to be unstable in solution[34], and thus the rate of decomposition may be related to the platinum–acetylene bond strength. Solutions of

$Pt(PPh_3)_2(PhC\equiv CH)$ deteriorate within a few hours whereas solutions of the dicyanoacetylene complex are stable for days. Suffice it to say, that criteria such as $\Delta\nu(C\equiv C)$ values and chemical reactivity are imperfect, and therefore perhaps sometimes contradictory, means of judging the relative stabilities of metal–acetylene complexes.

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