Acetylene Complexes of Iridium and Rhodium[1,2]

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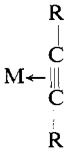
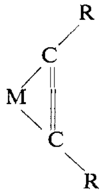
Abstract: A series of mononuclear acetylene complexes has been prepared from iridium(I) and rhodium(I) compounds. Provisional structures have been assigned to these 1:1 complexes based on their infrared spectra. Each type of mononuclear acetylene complex previously described in the literature is illustrated in the series of iridium complexes.

Transition metal–acetylene complexes have been described in scattered publications over the past 17 years. Such complexes are considered to be intermediates in metal-catalyzed cyclooligomerizations[4,5] and polymerizations[5,6] of acetylenes. Mononuclear acetylene complexes of vanadium,[7] tungsten,[8] rhenium,[9] manganese,[10,11] iridium,[12] nickel,[13] and platinum[14,15] have been prepared. Detailed X-ray diffraction studies of mononuclear acetylene complexes have not been reported. Provisional structures have been suggested on the basis of infrared stretching frequencies assigned to the coordinated acetylenes. Coordination by a transition metal has been shown to lower the acetylenic stretching frequency by 130 to 500 cm^{-1} from the range 2260–2190 cm^{-1}, normally exhibited[16] by disubstituted acetylenes. It has been implied that transition metal complexes of disubstituted acetylenes exhibit two extreme bond types, I and II.


I


II

In structures such as I the acetylene is thought to act as a monodentate ligand bonding to the metal in a manner similar to olefin complexes.[15] Such "π-bonded" complexes exhibit acetylene stretching frequencies 130 to 200 cm^{-1} lower than the free acetylenes. In the instance of coordinated symmetrical acetylenes the perturbed infrared absorption is often of weak intensity. The stoichiometry of π-bonded complexes is such that each acetylene is considered as a monodentate ligand in order to preserve the coordination number commonly associated with the metal in a reasonable oxidation state. It is implied[15] that complexes of the π-bonded type are stabilized by electron-releasing substituents on the acetylene or by adjacent hydroxyl groups which can form hydrogen bonds[17] with the unsaturated metal. Such intramolecular hydrogen bonding would not be possible if the angular geometry of the acetylene were distorted as in II. It is thus inferred that the geometry of the free acetylene is not greatly altered in this type of complex. Certainly the relatively small shift in the infrared frequency suggests a weakly perturbed triple bond.

In other instances disubstituted acetylene groups are so strongly affected by coordination to a transition metal that the triple-bond stretching frequency is lowered by ~500 cm^{-1}.[18] Complexes of this type have been described as "doubly σ-bonded,"[9,12,18,19] and it has been suggested that these coordinated acetylenes exhibit strong angular distortion as depicted in II. The angular disposition of the substituent groups is thought to be similar to a *cis* olefin. The multiple bond stretching frequencies around 1700 cm^{-1} for such complexes have been compared[12] to small ring endocyclic olefins. The acetylenes in complexes such as II are considered to behave as bidentate, chelating ligands. Electron-withdrawing substituents are thought to stabilize "doubly σ-bonded" acetylene complexes.[19] Precedents for dramatic alteration of acetylenic bond angles from 180 to ~120° and of bond lengths from 1.20 to >1.4 A can be found among X-ray diffraction studies of di- and trinuclear acetylene complexes.[20–22] However, to our knowledge the detailed structures of mononuclear acetylenes have not been determined.

At the present time it is an unsettled question as to whether the two bond types I and II represent energy minima and could be found in valence tautomerism or

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[2] A portion of this work was presented to the Second International Symposium on Organometallic Chemistry, Madison, Wis., Sept 1965, Abstracts, p 18.

[3] Fellow of the Alfred P. Sloan Foundation.

[4] G. N. Schrauzer, *Angew. Chem. Intern. Ed. Engl.*, **3**, 185 (1964).

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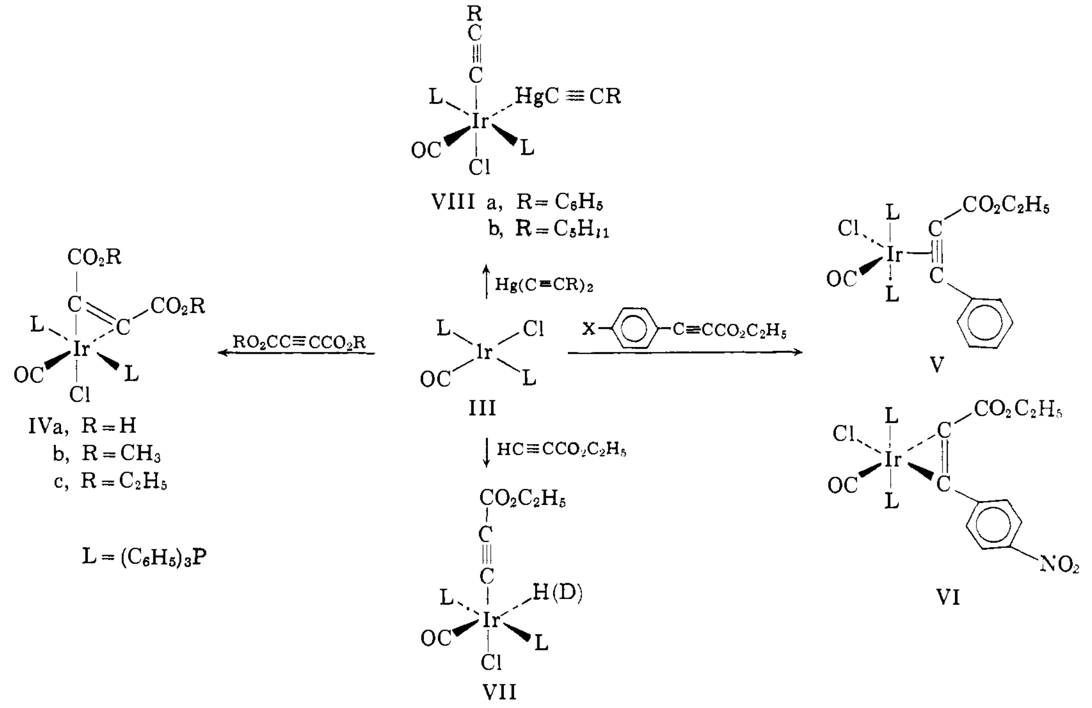
Scheme I



whether these are extreme descriptions of a gradual transformation. The reported infrared stretching frequencies among coordinated acetylenes are scattered over the range 2060 to 1600 cm^{-1}, suggesting a gradual change rather than two distinct bond types.

An additional type of acetylene complexes are the terminally bound metal acetylides.[23] These are usually formed by metathetical displacement of metal halides by ionic acetylides but are also considered to be formed as intermediates during the polymerization of terminal acetylenes by nickel(0) catalysts.[6]

Vaska's[24] unsaturated iridium(I) complex III (Scheme I) is characterized by its ability to add a fifth ligand such as CO[25] or ethylene[26] and to combine with a myriad of reagents to yield hexacoordinate formally iridium(III) compounds.[27] The latter process, which has been referred to as oxidative addition, is general for complexes having a conceptual d^8 configuration.[27,28] These two reactions are distinguished only by notions of localized bonding and conventions of oxidation state. There seems to be no *a priori* reason to expect a distinct boundary between these two extreme descriptions. This dilemma has already been encountered in the oxygen adduct IX[29] which can be considered either five-coordinate iridium(I) or six-coordinate iridium(III). Further examples of the problem in designating oxidation states are to be found in complexes of III with hexafluorobutyne-2 and tetrafluoroethylene.[12]

Herein is reported a series of acetylene complexes prepared from compounds of iridium(I) and rhodium(I). All of the previously reported types of mononuclear acetylene complexes are illustrated within this series. Provisional structures have been assigned to these 1:1 complexes based on infrared and occasionally nmr spectra.

Discussion

Vaska's[24] iridium(I) complex III readily combines with carboxyl-substituted acetylenes to form 1:1 adducts. Although the stoichiometry of these complexes is firmly established, their detailed structures can only be inferred from infrared spectra and to a lesser extent from proton nmr spectra. X-Ray diffraction studies will be required to substantiate the tentative structures depicted in Scheme I.[30]

Acetylenedicarboxylic acid and its dimethyl and diethyl esters react with III to form complexes which are provisionally assigned the structure shown for IV (Figure 1). These complexes are characterized by an additional strong infrared band in the 1600–1800-cm^{-1} region (Table I). This band cannot be distinguished from the two ester or acid carbonyl absorptions which also occur in this region. Tentative assignments have been made in Table I by considering that the carbonyl or ester groups absorb in the usual range exhibited by conjugated organic molecules. The nmr spectra of the esters IVb indicate the presence of two chemically different esters. A similar result was found in the F^{19} spectrum of the hexafluoro-2-butyne–iridium complex reported by Parshall.[12] This complex was assigned a structure similar to IV. The two ester carbonyl frequencies exhibited by IV also reflect the different chemical environment experienced by the ester groups. This is accounted for by the divergent *trans* effects of the CO and Cl groups *trans* to the terminals of the acetylene in the quasi-octahedral complexes. The two phosphine ligands are thought to be *trans* because other studies using methylated phosphines have indicated that the phosphorus ligands in-

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(27) J. P. Collman and W. R. Roper, *ibid.*, **87**, 4008 (1965), and references therein.
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(30) Professor J. A. Ibers has begun an X-ray investigation of these acetylene–iridium complexes.

Table I. Infrared Spectra[a,b]

Compound	ν_{CO}	$\nu_{C\equiv C}$	ν_{CO_2R}	Miscellaneous
$IrCl(CO)L_2$	1950 vs			
$IrCl(CO)L_2{}^{*c}$	1950 vs			
$RhCl(CO)L_2$	1950 vs			
$IrCl(CO)L_2(HO_2CC\equiv CCO_2H)$	2005 vs	1600 vs	1720, 1675 s	
$IrCl(CO)L_2(CH_3O_2CC\equiv CCO_2CH_3)$	1980 vs	1770 s	1725, 1680 s	
$IrCl(CO)L_2(C_2H_5O_2CC\equiv CCO_2C_2H_5)$	1990 vs	1770 s	1720, 1680 s	
$IrCl(CO)L_2(C_6H_5C\equiv CCO_2C_2H_5)$	1990 vs	2060 s	1690 s	
$IrCl(CO)L_2(p\text{-}NO_2C_6H_4C\equiv CCO_2C_2H_5)$	1990 vs	1750 s	1680 s	1520, 1350 s (NO_2)
$IrCl(CO)L_2H(C\equiv CCO_2C_2H_5)$	2060 vs	2130 s	1680 vs	2125 m (Ir–H)
$IrCl(CO)L_2D(C\equiv CCO_2C_2H_5)$	2060 vs	2130 s	1680 vs	1565 m (Ir–D)
$IrCl(CO)L_2(HgC\equiv CC_6H_5)(C\equiv CC_6H_5)$	2040 vs	2120 s		
$IrCl(CO)L_2{}^*(CH_3O_2CC\equiv CCO_2CH_3)$	1980 vs	1770 s	1725 m, 1680 vs	
$IrCl(CO)L_2(HC\equiv CCO_2H)$	2040 vs	1650 m	1700 w, 1675 vs	
$IrCl(CO)L_2((NC)_2C\equiv C(CN)_2)$	2025 vs			2210 s (CN)
$IrCl(CO)L_2(C_4H_2O_3)^d$	2030 vs		1740, 1810 s	
$IrCl(CO)L_2(C_6H_{10})^e$	2040 vs			
$IrCl(CO)L_2(C_2H_5O_2CN{=}NCO_2C_2H_5)$	2060 vs		1630 w, 1600 s	
$RhCl(CO)L_2(HO_2CC\equiv CCO_2H)$	2075 vs	1600 s	1680, 1625 vs	
$RhCl(CO)L_2(HC\equiv CCO_2H)$	2060 vs	1640 vs	1690 s	
$IrClL_2(CH_3O_2CC\equiv CCO_2CH_3)$		1855 s	1700 vs	
$IrClL_2(C_6H_5COC\equiv CCOC_6H_5)$		1780 s	1615 vs	
$IrClL_2(C_6H_5C\equiv CC_6H_5)$		1850 s		
$IrClL_2(C_6H_5C\equiv CCO_2C_2H_5)$		1840 s	1670 vs	
$IrClL_2(p\text{-}NO_2C_6H_4C\equiv CCO_2C_2H_5)$		1830 s	1680 vs	

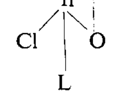
[a] All spectra reported are for KBr pellets. Solution spectra are very similar. Intensities of spectral bands are designated by vs (very strong), s (strong), m (medium), w (weak). [b] Frequencies reported in cm^{-1} measured on a grating instrument. [c] L represents triphenylphosphine and L* represents diphenylmethylphosphine. [d] Maleic anhydride complex. [e] Cyclohexene complex.

variably remain *trans* during oxidative additions.[31] An X-ray diffraction study of the oxygen adduct IX also shows *trans* phosphines.[29] The intensity of the infrared absorption exhibited by the symmetrical coordinated acetylene can also be accounted for by a dipole along the acetylene bond arising from the two different *trans* ligands. However, the probable distortion of the acetylenic bond angles from 180° could also account for an allowed infrared absorption.[10]

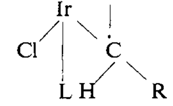
The wide variation in the tentatively assigned coordinated acetylene stretching frequencies is not surprising in view of the ranges of such absorptions reported for acetylene complexes involving different metals. The infrared spectra of IV as well as each of the other acetylene complexes bearing CO reveal a single very intense CO bond near 2000 cm^{-1}. It is now clear that the position of this absorption cannot be correlated with the formalism of oxidation state inasmuch as the position of this bond reflects both the electronegativity as well as the backbonding properties of the ligands.

Dialkylacetylenes fail to form stable complexes with III. Diphenylacetylene also does not form an isolable complex with III under the conditions employed. However, ethyl phenylpropiolate readily forms a 1:1 adduct (V) with III. The infrared spectrum of this complex is quite different from the spectra described above (Table I). In addition to the intense sharp absorption of the CO group at 1990 cm^{-1}, a strong band appears at 2060 cm^{-1}. In the region between 1600 and 1990 cm^{-1} only a single strong absorption appears at 1690 cm^{-1} and is assigned to the ester group. It would seem that the band at 2060 cm^{-1} should be assigned to a more weakly bound acetylene. Uncoordinated ethyl phenylpropiolate exhibits a strong triple bond stretching band at 2230 cm^{-1}. Thus complex formation caused a lowering of only 170 cm^{-1}, a figure similar to that reported by Chatt, *et al.*,[15,32] for the so-called π-bonded acetylene complexes of platinum(II). The complex proved too insoluble for its nmr spectrum to be measured. On the basis of this infrared spectrum the ethyl phenylpropiolate complex is assigned the structure depicted for V. It should be emphasized that this structure may prove indistinguishable from structures such as VI.

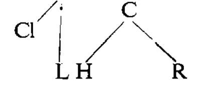
Limiting structures such as V resemble olefin complexes. We have prepared stable olefin complexes from III using tetracyanoethylene and maleic anhydride. Complexes were also derived from cyclohexene and diethyl azodicarboxylate, but these proved too labile for analyses. α-Methylmaleic anhydride failed to form an adduct with III, presumably because of increased steric hindrance. Previously a stable tetrafluoroethylene[12] complex and an unstable ethylene[29] complex were prepared from III. The infrared frequencies of the CO group in each of the olefin adducts (Table I) are little different from the CO frequencies exhibited by the acetylene complexes. The olefin complexes can also be considered to have two limiting structures, X and XI. With respect to the question of bonding, it would be interesting to compare the detailed structures of these olefin complexes with the structure of V.



IX



X



XI

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(31) C. T. Sears, Ph.D. Dissertation, University of North Carolina, 1966.

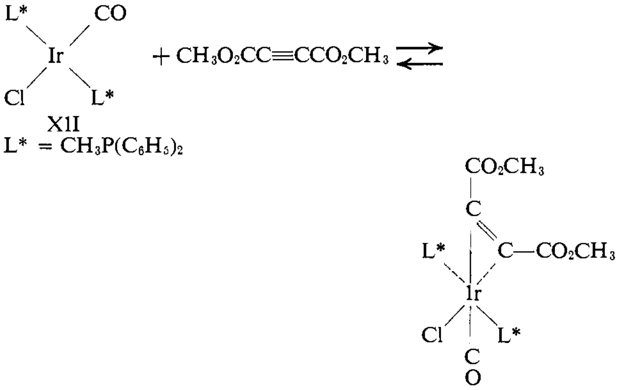
(32) J. Chatt, R. G. Guy, and L. A. Duncanson, *J. Chem. Soc.*, 827 (1961).

Chatt[18] had previously demonstrated that *p*-nitro substituents on phenylacetylenes greatly stabilize complexes of the so-called doubly σ-bonded or chelated type. With this in mind, we prepared a complex VI from III using ethyl *p*-nitrophenylpropiolate. The infrared spectrum of VI is dramatically different from that of V. The strong absorption at 2060 cm^{-1} has been replaced by a strong band at 1750 cm^{-1}. This latter band is assigned to the coordinated acetylene group. The position of this band is in the same area as in complexes IV, as well as certain acetylene complexes of Pt,[18] V,[7] Re,[9] W,[8] and Ir[12] reported elsewhere. The dramatic shift of 300 cm^{-1} caused by a *p*-nitro substituent suggests a change in bond type. X-Ray diffraction studies will be required to clarify this question.

Terminal acetylenes can react with III in a different manner. Treatment of III with ethyl propiolate yielded a complex formulated as VII in which the acetylenic carbon–hydrogen bond has been cleaved and a six-coordinate hydrido acetylide complex is formed. The structure (VII) assigned to this adduct is again based primarily on its infrared spectrum (Table I). A very strong, narrow band at 2060 cm^{-1} is assigned to the CO group which is *trans* to either a hydride or an acetylide. The *trans* effect of either of these ligands would account for the increase in frequency of the CO group. An intense band at 2130 cm^{-1} is assigned to the σ-bonded acetylide group. Support for this assignment comes from the mercury acetylide adducts VIII (Scheme I) derived from III by reactions analogous to the addition of mercuric halides[33] to III. Both of these adducts, as well as the free mercury acetylides, exhibit a strong band at 2130–2140 cm^{-1}. The iridium hydride peak is presumably obscured by either the CO peak at 2060 cm^{-1} or the acetylide peak at 2130 cm^{-1}. We consider the latter assignment more reasonable. Further evidence for an iridium–hydride bond stems from the deuteride complex. An infrared difference spectrum in which the hydride complex was placed in the reference cell and the deuteride complex in the sample cell revealed a medium intensity absorption at 1565 cm^{-1}. The nearby ester absorption was exactly compensated for. Additional support for structure VII was obtained by examining the nmr spectrum of this hydride. A single type of ethyl absorption was found but no peak was observed in the τ 7.08 region in which the acetylenic hydrogen signal is exhibited in the spectrum of the free ligand. Lack of available instrumentation prevented us from searching for the hydride peak at high field strength. A similar addition of acetylenic hydrogen bonds to nickel(0) complexes has been postulated to account for the polymerization of terminal acetylenes catalyzed by these nickel complexes.[5,6]

The reaction of III with propiolic acid is confusing. Initially a pale yellow crystalline complex, mp 247–249°, is formed. Elemental analyses indicate that this is a 1:1 adduct. However, careful examination of this product indicated the presence of two components. This material shows infrared bands at 2120, 2060, 1720, and 1660 cm^{-1}. The band at 2120 cm^{-1} suggests the presence of an isomer similar to VII. From the filtrate an apparently homogeneous complex was isolated as tan crystals, mp 253–254°. The infrared spectrum of this latter product exhibited bands at 2040, 1700, and 1625 cm^{-1}. We tentatively consider this complex to have a structure analogous to IV. Boiling the yellow crystalline mixture in toluene afforded the pure tan complex, mp 253–254°. These experiments suggest a tautomeric transformation.

The profound influence that substituent groups on the acetylenes have on the infrared spectra of acetylene complexes prompted us to examine the effect of changing the other ligands. Consequently, complex XII containing diphenylmethylphosphine in place of triphenylphosphine was prepared by ligand exchange. Diphenylmethylphosphine is thought to be a better σ donor but to have weaker back-bonding properties compared with triphenylphosphine. In another project we had found that XII combined more readily with alkyl halides than III.[31] To our surprise dimethyl acetylenedicarboxylate formed an easily dissociated complex XIII, which we were unable to thoroughly characterize.



XII

L* = $CH_3P(C_6H_5)_2$

XIII

It was also of interest to compare complexes derived from the rhodium(I) complex (XIV) with those iridium complexes discussed above. Acetylenedicarboxylic acid formed a stable complex (XV, Scheme II) whose infrared spectrum resembles its iridium analog (IV) (Table I). However, the higher CO frequency of 2075 cm^{-1} found in the rhodium complex as compared with the value of 2005 cm^{-1} for the iridium analog is surprising. Again the coordinated acetylene appears to absorb at 1600 cm^{-1}. It is possible that the carboxylic hydrogens are interacting with iridium, but it is difficult to see how this could be an intramolecular interaction.

Dimethyl acetylenedicarboxylate did not form an isolable complex with XIV but was catalytically trimerized to hexa(carbomethoxy)benzene (XVI). In a similar fashion, ethyl propiolate was trimerized to a mixture of 1,3,5- and 1,2,4-tri(carbomethoxy)benzenes (XVII and XVIII). Again the unreacted rhodium compound (XIV) was recovered. On the other hand, propiolic acid reacted with XIV to form a complex formulated as XIX as well as a small amount of trimesic acid (XX). It seems likely that complexes such as XIX are intermediates in these trimerization reactions and that these complexes react with a second mole of acetylene to form hypothetical complexes such as XXI containing a diene doubly σ-bonded to the metal. A similar mechanism has previously been proposed[34]

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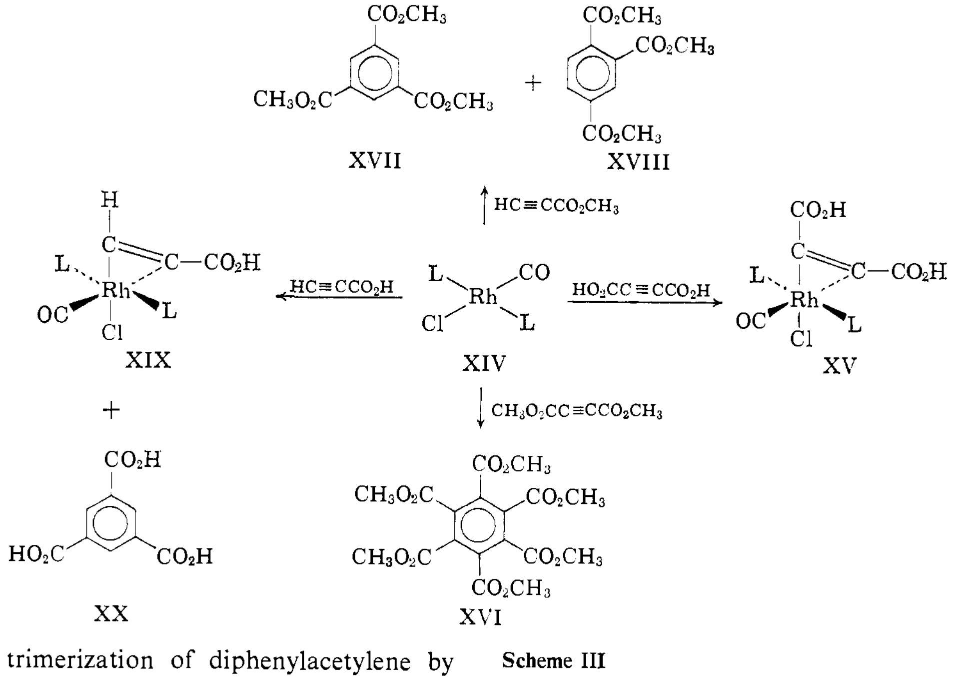
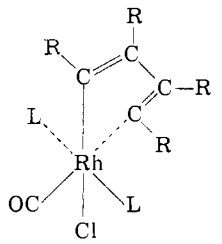
[33] R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 5337 (1965).

[34] A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962).

Scheme II



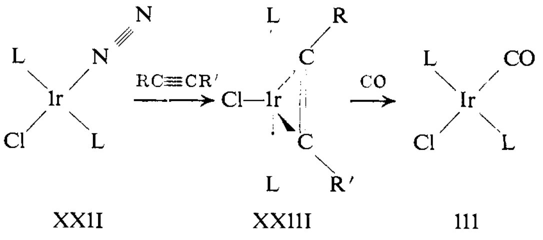
to explain the trimerization of diphenylacetylene by palladium(II). Furthermore a stable iron complex similar to XXI has been prepared by Bayer.[35] Trimerization mechanisms such as those suggested by Schrauzer[5,36] seem less likely in these cases inasmuch as coordination numbers higher than six would be required unless the strongly attached phosphines were to dissociate reversibly during these catalytic reactions. The reactions in Scheme II suggest that the acetylenecarboxylic acids form more stable complexes than the corresponding esters. However, the authors do not consider these experiments exact enough to merit this conclusion. These results do illustrate the tendency of iridium(I) to form more stable complexes than rhodium(I).



XXI

A further class of iridium–acetylene compounds has been derived from the recently discovered iridium complex of molecular nitrogen (XXII).[37] Treatment of XXII with a series of electronegatively disubstituted acetylenes afforded 1:1 crystalline adducts (XXIII) (Scheme III). In certain instances complexes of substituted cyclobutadiene are also formed, but these will be described elsewhere. These acetylene adducts may be formulated as five-coordinate trigonal-bipyramidal complexes of iridium as depicted in XXIII. They are characterized by intense infrared bands in the region of 1850 to 1780 cm^{-1} which are assigned to a coordinated acetylene. Proton nmr spectra of the symmetrical compounds such as XXIIIa reveal a single type of carboxylic ester, and this is supported by the single ester stretching mode in its infrared spectrum. Again it is controversial as to whether two σ bonds should be drawn from the ends of the acetylene to iridium (formal oxidation state iridium(III)) or a π bond to the acetylene. These two descriptions probably involve only valence-bond semantics. It is difficult to account for the relative frequencies of complexed acetylenes of the types IV and XXIII except to say that the latter are probably more strongly bound to iridium. Back-bonding effects are different because of the presence of CO in IV.

Scheme III



a, R = R′ = CH_3O_2C
b, R = R′ = C_6H_5CO
c, R = R′ = C_6H_5
d, R = C_6H_5; R′ = $CO_2C_2H_5$
e, R = p-$NO_2C_6H_4$; R′ = $CO_2C_2H_5$

Bulky acetylenes such as diphenylacetylene form complexes of type XXIIIc, whereas they do not form an isolable complex with III. It occurred to us that there was a possible indirect route to prepare a carbonyl complex of diphenylacetylene. It was anticipated that treatment of XXIII with CO should afford complexes analogous to IV. To our surprise reaction of XXIIIa with CO at atmospheric pressure yielded Vaska's compound III in every instance. This is most surprising inasmuch as a very reasonable transition state for this displacement should look like the complex IVb previously characterized. Furthermore it was found that IVb is stable to CO under these conditions.

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(35) E. Bayer, H. Brune, and K. L. Hock, *Angew. Chem.*, **74**, 872 (1962).

(36) G. N. Schrauzer, *Angew. Chem. Intern. Ed. Engl.*, **3**, 185 (1964).

(37) J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **88**, 3459 (1966).

In summary all of the previously described types of mononuclear acetylene complexes derived from transition metals can be prepared from Vaska's versatile iridium complex III. The characterization of such acetylene compounds by their infrared spectra is equivocal. The questions of bonding in these systems can only be answered through detailed structure determination.

Experimental Section

Iridium trichloride trihydrate and rhodium trichloride trihydrate were purchased from Engelhard Co. Acetylenedicarboxylic acid, dimethyl acetylenedicarboxylate, diethyl acetylenedicarboxylate, propiolic acid, ethyl propiolate, and diphenylacetylene were obtained from the Aldrich Chemical Co. Ethyl *p*-nitro-phenylpropiolate[38] and di(heptynyl)mercury[39] were prepared by known procedures.[38,39] Chlorocarbonylbis(triphenylphosphine)rhodium(I) was prepared by the method of Heck.[40]

All melting points were determined on a micro hot-stage apparatus and are uncorrected. Infrared spectra were obtained from Perkin-Elmer Model 237B and 421B grating spectrophotometers. Each spectrum was calibrated with a polystyrene film. A Varian A-60 spectrometer was used for measurement of the nmr spectra. Molecular weights were determined using a Mechrolab vapor pressure osmometer in benzene. All reactions were carried out under a nitrogen atmosphere.

Chlorocarbonylbis(triphenylphosphine)iridium(I) (III) Method A. In a 500-ml pressure bottle was placed 3 g of iridium trichloride trihydrate and 30 ml of methanol. The bottle was flushed several times with carbon monoxide, and then the carbon monoxide pressure was raised to 30 psi. The mixture was heated at 65° and stirred magnetically for 15 hr. The carbon monoxide pressure was vented and a solution of 6 g of triphenylphosphine in 30 ml of acetone was added to the contents of the pressure bottle. The solution was heated at 70° for 30 min during which carbon monoxide was evolved. The slurry was placed in a rotatory evaporator and the solvent removed. The yellowish white solid residue was placed in 150 ml of dimethylformamide and heated under reflux for 20 hr in a nitrogen atmosphere. To the cooled solution was added 300 ml of methanol. Lemon-yellow crystals were collected on a filter, yield 5.8 g (90%). The infrared spectrum was identical with that of an authentic sample of III prepared by the method of Vaska.[24]

Method B. A mixture of 3.52 g of iridium trichloride trihydrate and 13.1 g of triphenylphosphine in 150 ml of dimethylformamide was heated at reflux under nitrogen for 12 hr. The yellow solution was allowed to cool and combined with 300 ml of methanol. After cooling 7.0 g of yellow crystals of III were collected on a filter and washed with methanol.

Chlorocarbonylbis(diphenylmethylphosphine)iridium(I) (XII). To a solution of Vaska's iridium complex III (3 g, 0.384 mmole) in 100 ml of benzene was added 2.1 ml of diphenylmethylphosphine. The solution was heated under reflux for 10 min and then the solvent was removed under vacuum to yield a bright orange oil. To this residue was added 100–125 ml of *n*-hexane, and the mixture was heated at reflux under nitrogen for 1 hr. The mixture was cooled, and the yellow solid was collected on a filter. Recrystallization from benzene–methanol afforded 1.93 g (76%) of the yellow crystalline product. *Anal.* Calcd. for $C_{27}H_{26}ClOP_2Ir$: C, 49.35; H, 3.99; Cl, 5.40; P, 9.44. Found: C, 49.67; H, 4.02; Cl, 5.05; P, 9.18.

Chlorocarbonylbis(triphenylphosphine)(acetylenedicarboxylic acid)iridium (IVa). To a solution of the iridium(I) complex III (200 mg, 0.026 mmole) in 30 ml of benzene was added a solution of acetylenedicarboxylic acid (100 mg, 0.88 mmole) in 20 ml of benzene with stirring under nitrogen. After 1 hr the pale yellow precipitate was collected on a filter, washed with benzene and ether, and then dried over anhydrous calcium chloride in a vacuum desiccator. The pale yellow complex IVa weighed 210 mg (91%), mp >300° dec. *Anal.* Calcd for $C_{41}H_{32}O_5ClP_2Ir$: C, 55.03; H, 3.58. Found: C, 54.71; H, 3.78.

Chlorocarbonylbis(triphenylphosphine)(dimethyl and diethyl acetylenedicarboxylate)iridium (IVb and c). To a suspension of the iridium(I) complex III (320 mg, 0.041 mmole) in 20 ml of benzene was injected 600 mg (0.42 mmole) of dimethyl acetylenedicarboxylate under nitrogen. The brown solution was stirred for 1 hr. Removal of the solvent under vacuum afforded pale yellow crystals. Recrystallization of the crude adduct from benzene–methanol yielded 320 mg (90%) of the pure adduct IVb, mp 181–183° dec. *Anal.* Calcd. for $C_{43}H_{36}O_5ClP_2Ir$: C, 55.97; H, 3.89; mol wt, 922. Found: C, 55.77; H, 3.85; mol wt, 907.

The diethyl acetylenedicarboxylate adduct IVc was prepared in the same way, 87% yield, mp 152–155° dec. *Anal.* Calcd for $C_{45}H_{40}O_5ClP_2Ir$: C, 56.84; H, 4.21; mol wt, 950. Found: C, 56.47; H, 4.24; mol wt, 933.

Chlorocarbonylbis(triphenylphosphine)(ethyl phenylpropiolate)iridium (V). A mixture of the iridium(I) complex III (300 mg, 0.03 mole) and 5 ml of ethyl phenylpropiolate was heated at 100° and stirred under nitrogen for 24 hr. The reaction mixture was cooled and combined with 30 ml of methanol. The solid precipitate was collected on a filter and washed with methanol. The crude tan product was recrystallized from methylene chloride–methanol yielding 240 mg (65%) of fine tan crystals of V, mp 214–216° dec. *Anal.* Calcd for $C_{48}H_{40}ClP_2Ir$: C, 60.38; H, 4.19; mol wt, 954. Found: C, 59.89; H, 4.20; mol wt, 938.

Chlorocarbonylbis(triphenylphosphine)(ethyl *p*-nitrophenylpropiolate)iridium (VI). To a solution of the iridium(I) complex III (500 mg. 0 064 mmole) in 10 ml of chloroform was added a solution of ethyl *p*-nitrophenylpropiolate (150 mg, 0.068 mmole) in 5 ml of chloroform at room temperature. The orange-yellow solution was stirred at 50° for 3 hr and then cooled in a refrigerator. The resulting yellow crystals were collected, washed with ether, dried under vacuum, and recrystallized from chloroform–ethanol (2:1) affording 540 mg (83%) of pure VI, mp 182–185° dec. *Anal.* Calcd for $C_{48}H_{39}NO_5ClP_2Ir$: C, 57.66; H, 3.90; P, 6.21; mol wt, 999. Found: C, 57.39; H, 3.72; P, 6.02; mol wt, 972. The infrared spectrum of VI exhibited strong bands at 1990, 1750, 1680, 1600, 1520, and 1350 cm^{-1}.

Chlorohydridocarbonylbis(triphenylphosphine)(carboxyethylacetylide)iridium(III). To a suspension of the iridium(I) complex (500 mg, 0.064 mmole) in 50 ml of benzene under nitrogen was injected ethyl propiolate (600 mg, 0.7 mmole). The mixture was stirred for 15 hr at 50°. The solvent was removed under vacuum and the residual oil dissolved in 95% ethanol. The ethanol solution was filtered and then evaporated under vacuum. Recrystallization of the crude solid from 95% ethanol afforded 510 mg (92%) of the pure adduct VII, mp 150–152° dec. The nmr spectrum revealed signals at τ 8.9 (triplet), 6.1 (quartet), and 2.6 (complex doublet) in a ratio of 3:2:30. *Anal.* Calcd for $C_{42}H_{36}O_3ClP_2Ir$: C, 57.47; H, 3.99; mol wt, 878. Found: C, 57.56; H, 4.31; mol wt, 870.

Addition of Propiolic Acid to Chlorocarbonylbis(triphenylphosphine)iridium(I). To a solution of the iridium(I) complex III (500 mg, 0.064 mmole) in 30 ml of benzene under nitrogen was injected propiolic acid (450 mg, 0.064 mmole) at 50°. The reaction mixture was stirred for 3 hr and then the solvent was removed under vacuum. The residual oil was taken up in 30 ml of 95% ethanol and allowed to stand at room temperature until pale yellow crystals formed. These crystals were collected and recrystallized from 95% ethanol affording 240 mg of fine pale yellow crystals, mp 247–249° dec. The infrared spectrum (KBr) of this product exhibits bands at 2120 (m), 2060 (vs), 1720 (s), and 1660 (s) cm^{-1}. *Anal.* Calcd for $C_{41}H_{32}O_3ClP_2Ir$: C, 56.47; H, 3.76; mol wt, 850. Found: C, 56.20; H, 3.81; mol wt, 843.

The filtrate was concentrated to about 5 ml and allowed to stand, whereupon fine tan crystals were formed. Recrystallization of the tan complex from 95% ethanol afforded 250 mg of tan crystals, mp 253–254° dec. The infrared spectrum (KBr) of this product exhibits bands at 2040 (vs), 1700 (m), and 1625 (s) cm^{-1}. *Anal.* Calcd for $C_{41}H_{32}O_3ClP_2Ir$: C, 56.47; H, 3.76; mol wt, 850. Found: C, 56.40; H, 4.00; mol wt, 858.

The pale yellow crystalline product (200 mg) was boiled in toluene for 1 hr. Removal of the solvent under vacuum and recrystallization of the crude product from 95% ethanol afforded 180 mg of fine tan crystals, mp 253–254° dec. The infrared spectrum of this material is identical with that described above.

Addition of Diphenylethynylmercury to Chlorocarbonylbis(triphenylphosphine)iridium(I). To a solution of the iridium(I) complex III (300 mg, 0.038 mmole) in 50 ml of methylene chloride under nitrogen was injected slowly a solution of diphenylethynylmercury (155 mg, 0.038 mmole) in 10 ml of methylene chloride. The reaction mixture immediately changed from yellow to deep purple. The mixture was heated under reflux for 1 hr. The solvent was removed under vacuum and the solid residue extracted with 50

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(38) V. B. Drewsen, *Ann.*, **212**, 156 (1882).

(39) J. R. Johnson and W. L. McEiven, *J. Am. Chem. Soc.*, **48**, 469 (1926).

(40) R. F. Heck, *ibid.*, **86**, 2796 (1964).

ml of ether. Evaporation of the ethereal extract afforded a crude product which was further purified by recrystallization from ether–ethanol, yield 410 mg (90%) of red-purple crystals of VIIIa, mp 172–175° dec. *Anal.* Calcd for $C_{53}H_{50}OClP_2HgIr$: C, 53.76; H, 3.38; mol wt, 1183. Found: C, 53.45; H, 3.79; mol wt, 1174.

Addition of Di-*n*-heptynylmercury to Chlorocarbonylbis(triphenylphosphine)iridium(I). By the same procedure described above the crude product was obtained from the reaction of the irridum(I) complex III (300 mg, 0.038 mmole) with di-*n*-heptynylmercury (151 mg, 0.038 mmole). After two crystallizations of the crude product from ethanol, 335 mg (74% yield) of the pure adduct VIIIb was obtained as pale yellow crystals, mp 144–145° dec. *Anal.* Calcd for $C_{51}H_{52}OClP_2HgIr$: C, 52.26; H, 4.44; mol wt, 1171. Found: C, 51.80; H, 4.43; mol wt, 1154.

Addition of Dimethyl Acetylenedicarboxylate to XII. To a solution of XII (300 mg, 0.046 mmole) in 10 ml of benzene was added a solution of dimethyl acetylenedicarboxylate (300 mg, 0.21 mmole) in 5 ml of benzene at room temperature. The pale yellow solution was stirred for 1 hr and the solvent was removed under vacuum. Washing the residue with ether gave pale yellow solid (XIII), which was collected on a filter. The infrared spectrum of this solid revealed strong bands at 1980, 1760, and 1680 cm^{-1}. A medium intensity band was found at 1725 cm^{-1}. Attempts to recrystallize XIII from benzene–methanol or chloroform–methanol yielded XII.

Chlorocarbonylbis(triphenylphosphine)(maleic anhydride)iridium. To a solution of the iridium(I) complex III (200 mg, 0.025 mmole) in 20 ml of chloroform was added a solution of maleic anhydride (100 mg, 0.1 mmole) in chloroform. The reaction mixture was stirred for 1 hr, the solvent removed under vacuum, and the residue washed with ether. Recrystallization in chloroform–ether at 5° (the compound decomposes to starting materials at higher temperatures) afforded 200 mg (89%) of nearly pure adduct as pale yellow crystals, mp 172–173° dec. The adduct exhibits (selected) infrared peaks at 2030 (vs), 1960 (w), 1810 (vs), 1565 (w), and 1585 (w) cm^{-1}. *Anal.* Calcd for $C_{41}H_{32}O_4ClP_2Ir$: C, 56.04; H, 3.64; mol wt, 878. Found: C, 55.49; H, 3.88; mol wt, 851.

Chlorocarbonylbis(triphenylphosphine)(tetracyanoethylene)iridium. To a solution of the iridium complex III (300 mg, 0.038 mmole) in 5 ml of chloroform was added tetracyanoethylene (50 mg, 0.039 mmole) at room temperature. The reaction mixture was stirred for 1 hr, during which white crystals slowly precipitated from the solution. The crystals were collected, washed with ethanol, dried under vacuum, and then recrystallized from chloroform–ethanol, yield 320 mg (19%). *Anal.* Calcd for $C_{43}H_{30}ClN_4OP_2Ir$: C, 56.21; H, 3.27; N, 6.10; mol wt, 918. Found: C, 56.02; H, 3.51; N, 6.22; mol wt, 908. Selected strong infrared peaks were found at 2110 and 2025 cm^{-1}.

Chlorocarbonylbis(triphenylphosphine)(acetylenedicarboxylic acid)rhodium(III) (XV). To a solution of the rhodium(I) complex XIV (500 mg, 0.076 mmole) in 50 ml of benzene under nitrogen was injected a solution of acetylenedicarboxylic acid (500 mg, 0.520 mmole) in 20 ml of benzene at 80° with stirring. The mixture was stirred for 1 hr at 80° and then filtered, and the residues were washed with hot benzene. The combined filtrates were washed under vacuum. After the residue was treated with 95% ethanol, the insoluble yellow crystals were collected on a filter to give 220 mg of the starting material (XIV). The ethanol filtrate was evaporated under vacuum. Recrystallization of the residue from 95% ethanol afforded 218 mg (64% yield) of the pure adduct XV as pale yellow crystals, mp 205–207° dec. *Anal.* Calcd for $C_{41}H_{32}O_5ClP_2Rh$: C, 61.12; H, 3.98; mol wt, 805. Found: C, 60.92; H, 4.02; mol wt, 788.

Reaction of Chlorocarbonylbis(triphenylphosphine)rhodium(I) with Propiolic Acid. To a solution of the rhodium(I) complex XIV (300 mg, 0.045 mmole) in 50 ml of benzene under nitrogen was injected propiolic acid (100 mg, 0.14 mmole). After the mixture was stirred for 1 hr at 25°, the brown solution was filtered and the solid washed with benzene. The combined benzene filtrates were evaporated under vacuum to give an oily residue. The oily residue was taken up in a small volume of ether and combined with methanol to yield a brown solid. Recrystallization of the brown solid from methanol afforded 140 mg (37% yield) of the adduct XIX as tan crystals, mp 180–181° dec. *Anal.* Calcd for $C_{40}H_{31}O_3ClP_2Rh$: C, 65.66; H, 4.37; mol wt, 731. Found: C, 65.28; H, 4.49; mol wt, 719.

The solid precipitate was treated with ethanol and filtered to remove an unknown polymer which was washed with ethanol. The combined ethanol filtrates were evaporated under vacuum to give a pale yellow solid. Recrystallization of this crude product from 95% ethanol afforded 46 mg of trimesic acid characterized by comparison of its melting point and infrared spectrum with those of an authentic sample.

Reaction of Chlorocarbonylbis(triphenylphosphine)rhodium(I) with Ethyl Propiolate. To a solution of the rhodium(I) complex (300 mg, 0.045 mmole) in 25 ml of benzene was added ethyl propiolate (1.0 g, 1 mmole). After the brown solution was stirred for 15 hr the mixture was reduced to dryness under vacuum. The dark brown residue was treated with 50 ml of 95% ethanol, and the resulting yellow solid was collected on a filter and washed with ethanol to yield 280 mg of the rhodium(I) complex XIV. The combined filtrates were concentrated to 15 ml and upon cooling in the refrigerator pale yellow crystals separated. These were collected and recrystallized from 95% ethanol to yield 260 mg of 1,3,5-tris(carbethoxy)benzene as colorless crystals. This substance was identified by its infrared and nmr spectra and by elemental analysis. *Anal.* Calcd for $C_{15}H_{18}O_6$: C, 61.22; H, 6.12. Found: C, 60.82; H, 5.98.

The filtrate was evaporated under vacuum and the oily residue distilled at 120–130° (0.05 mm). The colorless distillate was redistilled at 144–145° (0.2 mm) to afford 930 mg of 1,2,4-tris(carbethoxy)benzene, identified by its infrared and nmr spectra and elemental analysis. *Anal.* Calcd for $C_{15}H_{18}O_6$: C, 61.22; H, 6.12. Found: C, 61.50; H, 6.08.

Reaction of Chlorocarbonylbis(triphenylphosphine)rhodium(I) with Dimethyl Acetylenedicarboxylate. To a solution of the rhodium(I) complex XIV (300 mg, 0.045 mmole) in 25 ml of benzene was added dimethyl acetylenedicarboxylate (500 mg) at 80°. After the mixture was heated at reflux for 15 hr the solution was reduced to dryness under vacuum. The residue was treated with ethanol, and the resulting yellow crystalline starting material XIV was collected on a filter, yield 286 mg. The combined ethanol filtrates were evaporated under vacuum. The crude product was recrystallized from benzene–methanol to afford 435 mg (86% yield) of hexa(carbomethoxy)benzene. The infrared spectrum and melting point were identical with those of an authentic sample. *Anal.* Calcd for $C_{18}H_{18}O_2$: C, 50.71; H, 4.22. Found: C, 50.89; H, 4.32.

Reaction of Chlorocarbonylbis(triphenylphosphine)iridium(I) with Phenylacetylene. A solution of the iridium(I) complex III (250 mg, 0.032 mmole) in 30 ml of benzene was stirred with phenylacetylene (620 mg, 0.600 mmole) at 80° for 15 hr. The brown solution was evaporated to dryness under vacuum. The residue was dissolved in chloroform and anhydrous hydrochloric acid was passed through the chloroform solution until no more white precipitate was formed. The white solid was collected on a filter and washed with chloroform to give 260 mg of trichlorocarbonylbis(triphenylphosphine)iridium(III), identified by comparing its infrared spectrum with that of an authentic sample.

The combined filtrates were evaporated under vacuum to afford a yellow solid. Reprecipitations of this amorphous solid from chloroform–methanol afforded 360 mg of a product whose infrared spectrum was similar to that of polyphenylacetylene reported by Okamoto.[41] *Anal.* Calcd for $(C_8H_6)_n$: C, 94.18; H, 6.86. Found: C, 91.99; H, 7.76.

Chlorobis(triphenylphosphine)(dimethyl acetylenedicarboxylate)iridium (XXIIIa). To a suspension of the nitrogen complex XXII[37] (400 mg, 0.051 mmole) in 10 ml of acetone was added dimethyl acetylenedicarboxylate (150 mg, 0.106 mmole) at 10° under nitrogen. Nitrogen evolved and a yellow solid was formed. The crude yellow product (380 mg, 81%) was collected on a filter. Recrystallization from chloroform–methanol afforded 350 mg of the pure yellow crystalline complex XXIIIa, mp 182–183° dec. *Anal.* Calcd for $C_{42}H_{36}ClO_4P_2Ir$: C, 56.37; H, 4.03; Cl, 4.03; P, 6.82; mol wt, 894. Found: C, 56.09; H, 4.15; Cl, 4.21; P, 6.69; mol wt, 864.

Chlorobis(triphenylphosphine)(dibenzoylacetylene)iridium (XXIIIb). To a mixture of the nitrogen adduct XXII (500 mg, 0.064 mmole) and dibenzoylacetylene (150 mg, 0.064 mmole) was added 10 ml of benzene with stirring at room temperature under nitrogen. Nitrogen evolved immediately and a violet solution resulted. This solution was heated under reflux for 1 hr and then evaporated under vacuum, yielding a crude purple solid (520 mg, 82%). Recrystallization from benzene–methanol afforded 490 mg of pure crystalline product XXIIIb, mp 170–172° dec. *Anal.* Calcd for $C_{52}H_{40}O_2ClP_2Ir$: C, 63.29; H, 4.05; Cl, 3.65; P, 6.21; mol wt, 986. Found: C, 63.05; H, 4.11; Cl 3.91; P, 6.13; mol wt, 979.

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(41) Y. Okamoto, A. Gardon, F. Movsovicius, H. Hellman, and W. Brenner, *Chem. Ind.* (London), 2004 (1961).

Chlorobis(triphenylphosphine)(diphenylacetylene)iridium (XXIIIc). To a mixture of the nitrogen complex XXII (500 mg, 0.064 mmole) and diphenylacetylene (200 mg, 0.112 mmole) was added under nitrogen 10 ml of benzene with stirring. After the brown solution had been stirred for 2 hr at 45°, an insoluble precipitate (10 mg) was removed by filtration. Evaporation of the filtrate under vacuum afforded a brown solid which was purified by recrystallization from benzene–methanol, yield 510 mg (85%) of yellow crystals, mp 193–195° dec. *Anal.* Calcd for $C_{50}H_{40}ClP_2Ir$: C, 64.52; H, 4.30; Cl, 2.79; P, 6.67; mol wt, 930. Found: C, 64.30; H, 4.39; Cl, 3.01; P, 6.50; mol wt, 896.

Chlorobis(triphenylphosphine)(ethyl phenylpropiolate)iridium (XXIIId). To a suspension of the nitrogen complex XXII (500 mg, 0.064 mmole) in 5 ml of benzene was added a solution of ethyl phenylpropiolate (150 mg, 0.086 mmole) in 5 ml of benzene under nitrogen at 10°. After the addition was complete the mixture was stirred for 1 hr at room temperature. The solvent was removed under vacuum to give an oily residue. The yellow crystalline product was obtained by crystallization from benzene–methanol, yield 480 mg (81%), mp 192–193° dec. *Anal.* Calcd for $C_{47}H_{40}ClO_2P_2Ir$: C, 60.91; H, 4.32; Cl, 3.89; P, 6.74; mol wt, 926. Found: C, 61.18; H, 4.16; Cl, 4.02; P, 6.48; mol wt, 899.

Chlorobis(triphenylphosphine)(ethyl *p*-nitrophenylpropiolate)iridium (XXIIIe). The purple crystalline complex XXIIIe was prepared in the manner outlined above, yield 570 mg (92%), mp 124–126° dec. *Anal.* Calcd for $C_{47}H_{39}ClNO_2P_2Ir$: C, 58.08; H, 4.02; Cl, 3.71; P, 6.38; mol wt, 971. Found: C, 57.89; H, 4.16; Cl, 3.99; P, 6.15; mol wt, 998.

Phosphorus Trioxide as a Tetradentate Ligand.
II. Borane Complexes

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Abstract: When diborane is slowly bubbled through a solution of P_4O_6 in dry chloroform at room temperature, P^{31} nuclear magnetic resonance shows that there is successive coordination of one, two, and three BH_3 groups around the P_4O_6. Crystalline species corresponding to $P_4O_6 \cdot 2BH_3$ and $P_4O_6 \cdot 3BH_3$ have been obtained. In solution, equilibria are reached rapidly between the various $P_4O_6 \cdot xBH_3$ complexes (where $x = 0, 1, 2, 3$, and 4) so that the distribution of species corresponding to any given BH_3/P_4O_6 mole ratio may be calculated from the set of three equilibrium constants presented herein. A fourth constant relates the partial pressure of diborane to the solution composition.

In paper I[2] and a prior brief communication,[3] it was shown that the P_4O_6 cage molecule acts as a tetradentate nonchelating ligand in the coordination chemistry of transition metals. This finding led to the investigation as to whether phosphorus trioxide would donate lone-pair electrons to Lewis acids. A communication from Japan[4] and one from our laboratory[5] attest to the fact that P_4O_6 reacts with B_2H_6 to give complexes in which BH_3 groups are coordinated around the P_4O_6 molecule. The purpose of this paper is to give a full account of the preparation and properties of the complexes formed between phosphorus trioxide and borane.

Experimental Section

Nmr Measurements. The P^{31}, B^{11}, and H^1 nuclear magnetic resonance (nmr) spectra were obtained at 40.5, 15.1, and 60.0 Mc, respectively, on Varian spectrometers HR-100, HR-60, and A-60. The P^{31} chemical shifts (presented in ref 5) were referenced with respect to P_4O_6, generally as an internal standard, but are reported with respect to 85% H_3PO_4. The H^1 (also see ref 5) and B^{11} chemical shifts are respectively referenced to dissolved tetramethylsilane and to $BF_3 \cdot O(C_2H_5)_2$ contained in a capillary. Upfield shifts are denoted with a positive sign.

Reagents and Reactions. The phosphorus trioxide and nickel carbonyl were the same as previously described,[2] and the diborane was obtained from the Callery Chemical Co., Pittsburgh, Pa. The reaction of P_4O_6 and B_2H_6 was carried out by first passing the diborane through a cold trap at −60° and then slowly bubbling it at a rate of *ca.* 10 ml/min into a 1:2 by volume solution of P_4O_6 in dry chloroform or *n*-hexane maintained at 25°. Samples were removed at regular intervals of time with a syringe through a serum-bottle stopper and transferred into 5-mm precision-bore nmr tubes in a glove bag under dry nitrogen. A number of admixing reactions, such as combining crystalline $P_4O_6 \cdot 2BH_3$ with P_4O_6, were carried out in the nmr tubes, adding dry chloroform when a solvent was needed. All handling operations were performed in a plastic dry bag flushed with dry nitrogen. *Warning:* The $P_4O_6 \cdot xBH_3$ compounds react explosively with water and moist air. Even old samples, minor spillings, etc., can sometimes produce unexpected firecracker-like explosions when present in small quantities.

Preparation of Crystalline $P_4O_6 \cdot 2BH_3$. The crystalline compound $P_4O_6 \cdot 2BH_3$ was prepared by slowly blowing diborane over the surface of pure P_4O_6 (3.04 g) at 25°. Crystals began to form after *ca.* 8 hr, and a solid crystalline mass resulted after 12 hr, at which time the P_4O_6 had been quantitatively transformed into $P_4O_6 \cdot 2BH_3$ (3.40 g). Recrystallization in dry *n*-pentane at Dry Ice temperature gave long transparent needles. The infrared spectrum obtained on a KBr pellet protected from moisture exhibited the characteristic B–H stretching absorption at 2400 cm^{-1}.[6]

Results and Conclusions

Reaction with Diborane. An exothermic reaction takes place when diborane is bubbled through a solution of P_4O_6 in an inert dry solvent without temperature control. The reaction mixture is seen to convert

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