$k_d \simeq 2.0 \times 10^3$ sec^{-1}, to obtain $a = k_d/[A]_0k_f = 0.128$ and $w = (1 + 2k_f[A]_0t) = 1 + (3.1 \times 10^4)t$. Using these parameters we estimate $[B] = 5.3 \times 10^{-6}$ *M* at 200 μsec; the measured absorbance (20 cm) was 0.083 so $\epsilon_D = 783$ cm^{-1} M^{-1}.

Appendix II. Final Stages of the Reaction of $Rh(NH_3)_5NH^{3+}$ with I^-

For the absorbance of iodine species at 404.7 nm at any time in a 20-cm cell, $A = 12.4 \times 10^4[I_3^-] + 4.9 \times 10^3[I_2]$. Thus $[I_2] = A/\{1.24 \times 10^5[I^-]K + 4.9 \times 10^3\}$ and $[I_3^-] = KA[I^-]/\{1.24 \times 10^5[I^-]/K + 4.9 \times 10^3\}$, so

$$[I_2]_T = [I_2] + [I_3^-] = \left\{\frac{1 + K[I^-]}{1.24 \times 10^5[I^-]K + 4.9 \times 10^3}\right\}A$$

where *A* has been found to be equal to $(44 \pm 6)[I^-]$. This final reaction stage is pseudo first order in $[I^-]$

$$d[I_2]_T/dt = k'[I^-][Rh(NH_3)_5NH^{3+}]$$

The value of $[I_2]_T$ at any time *t* may thus be represented by the equation in the text.

Registry No. $[Rh(NH_3)_5N_3](ClO_4)_2$, 15603-08-4; *trans*-$[Rh(NH_3)_4(N_3)_2]ClO_4$, 41137-82-0; $K_3[Co(CN)_5N_3]$, 14705-99-8.

Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002

Reactions of π-Cyclopentadienyldicarbonylrhodium and π-Cyclopentadienyldicarbonyliridium with Disubstituted Acetylenes[1]

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Received April 26, 1973

The reactions of π-cyclopentadienyldicarbonylrhodium (**1**) and diphenylacetylene (**2**) in refluxing xylene or toluene produce hexaphenylbenzene, in addition to several novel di- and trinuclear organorhodium complexes, many of which are analogous to those isolated from reactions of iron carbonyls with acetylenes. The catalytic behavior of **1** in the cyclotrimerization of **2** to hexaphenylbenzene has been demonstrated. Reactions of π-cyclopentadienyldicarbonyliridium with bis(pentafluorophenyl)acetylene have been observed to produce low yields of the trimerization product, hexakis(pentafluorophenyl)benzene, as well as several organoiridium compounds analogous to the newly isolated rhodium complexes.

Introduction

While reactions of π-cyclopentadienyldicarbonylcobalt with disubstituted acetylenes have been described extensively in the literature,[2-10] the analogous reactions of π-cyclopentadienyldicarbonylrhodium (**1**) have received little attention. Dickson[11] has reported the formation of several organorhodium complexes from the reaction of **1** with hexafluoro-2-butyne, including a dirhodium species containing a bridging acetylene.[12] Another product from this reaction, π-cyclopentadienyl[hexakis(trifluoromethyl)benzene]rhodium, was shown to represent the first example of an arene acting as a four-electron donor.[13]

We have recently reported that a reaction between **1** and bis(pentafluorophenyl)acetylene[14] produces a good yield of trimerized acetylene, hexakis(pentafluorophenyl)benzene, in addition to several new di- and trinuclear rhodium complexes. In light of the extensive trimerization of the acetylene, the catalytic behavior of **1** with acetylenes is currently under investigation.

The differences in rhodium *vs.* cobalt modes of interaction with acetylenes observed in compounds resulting from the above reactions prompted further investigations of reactions of **1** with other disubstituted acetylenes. Certain similiarities to iron carbonyl reactions with acetylenes were noted in our previous work[14] [$Fe(CO)_3$ and $(\pi\text{-}C_5H_5)Rh$ are isoelectronic], and Dahl[15] had formally compared the solution and solid-state structures of Fe_3CO_{12} to those of the known tris(π-cyclopentadienylcarbonylrhodium) isomers.[16-18] Thus, considering the increased strength of metal-metal bonds[19] as one descends a column of the periodic table, the formation of a number of other compounds analogous to the well-known acetylene-carbonyl-iron series[20] was recognized as a possibility. This bonding effect has already been demonstrated by a comparison of the chemistry of iron and ruthenium triangular derivatives of the type $M_3(CO)_{12}$.[19] However, more systematic work on studies of the second-row transition metals was needed to support these observations in the cobalt triad.

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[1] (a) Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 13-17, 1971; see Abstracts, No. INOR 163. (b) Presented in part at the Vth International Conference on Organometallic Chemistry, Moscow, U.S.S.R., Aug 16-21, 1971; *Pure Appl. Chem.*, 30, 523 (1972).

[2] A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Jap.*, 34, 452 (1961).

[3] M. D. Rausch and R. A. Genetti, *J. Amer. Chem. Soc.*, 89, 5502 (1967); *J. Org. Chem.*, 35, 3888 (1970).

[4] R. Markby, H. W. Sternberg, and I. Wender, *Chem. Ind.* (*London*), 1381 (1959).

[5] J. L. Boston, D. W. A. Sharpe, and G. Wilkinson, *J. Chem. Soc.*, 3488 (1962).

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[8] R. S. Dickson and P. Fraser, *Aust. J. Chem.*, 23, 2403 (1970).

[9] M. D. Rausch, I. Bernal, B. R. Davis, A. Siegel, F. A. Higbie, and G. Westover, *J. Coord. Chem.*, in press.

[10] H. Sakurai and J. Hayashi, *J. Organometal. Chem.*, 39, 365 (1972).

[11] R. S. Dickson and G. Wilkinson, *J. Chem. Soc.*, 2699 (1964).

[12] R. S. Dickson and H. P. Kirsch, *J. Organometal. Chem.*, 32, C13 (1971); *Aust. J. Chem.*, 25, 2535 (1972).

[13] M. R. Churchill and R. Mason, *Proc. Roy. Soc., Ser. A*, 292, 61 (1966).

[14] M. D. Rausch, P. S. Andrews, S. A. Gardner, and A. Siegel, *Organometal. Chem. Syn.*, 1, 289 (1971).

[15] C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 91, 1351 (1969).

[16] O. S. Mills and E. F. Paulus, *Chem. Commun.*, 815 (1966); *J. Organometal. Chem.*, 10, 331 (1967).

[17] E. F. Paulus, E. O. Fischer, H. P. Fritz, and H. Schuster-Woldan, *J. Organometal. Chem.*, 10, P3 (1967).

[18] E. F. Paulus, *Acta Crystallogr., Sect. B*, 25, 2206 (1969).

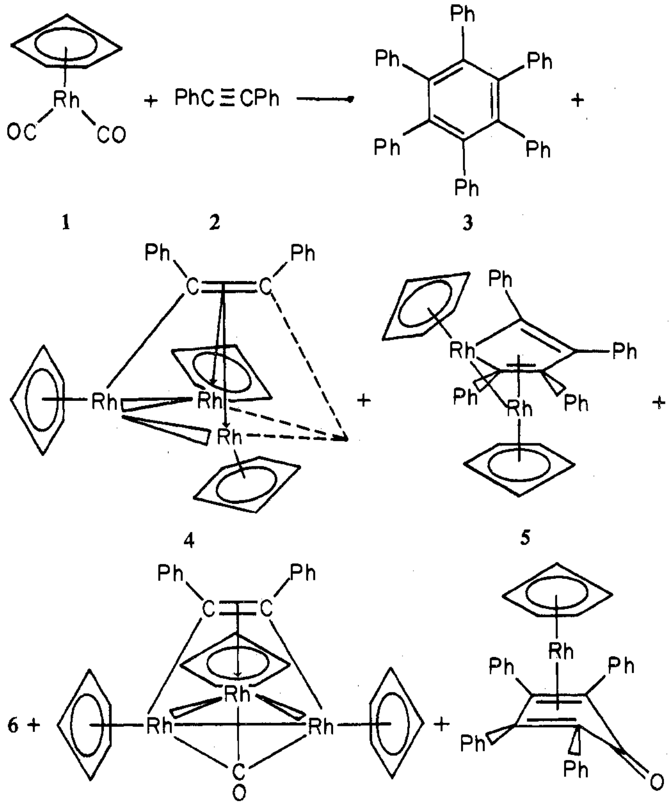
[19] R. B. King, *Progr. Inorg. Chem.*, 13, 287 (1972).

[20] W. Hubel in "Organic Synthesis *via* Metal Carbonyls," Vol. 1, Interscience, New York, N. Y., 1968, pp 273-342.

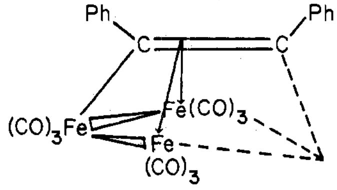
Results and Discussion

We now report that a reaction between **1** and diphenylacetylene (**2**) in refluxing xylene results in formation of the organic trimerization product, hexaphenylbenzene (**3**), in 55% yield, by far the major reaction product. Compound **3** was identified by a combination of elemental analysis and mass spectrometry. The catalytic trimerization of phenyl- and diphenylacetylene to substituted benzenes by $Rh_4(CO)_{12}$ has also recently been reported.[21]

In addition to **3**, the reaction between **1** and **2** also produces five highly colored organorhodium complexes, which were separated and purified by a combination of column chromatography, preparative tlc, and recrystallization techniques.

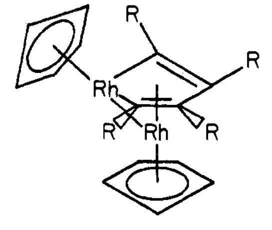


Complex **4**, diphenylacetylenetris(π-cyclopentadienylrhodium), was eluted first from the column and was isolated by preparative tlc as an orange-red solid. Compound **4** was assigned the structure shown above on the basis of elemental analysis and mass spectrometry (m/e 682). This formulation of compound **4** has precedence in the literature, since Dahl and coworkers[22] have confirmed such a structure for the iron analog **9**. A similiar representation of the bonding in **4** would then arise by regarding the acetylene fragment as a coordinated olefin with two normally π electrons placed in a σ-type sp^2 orbital on the carbon atom nearest the unique rhodium atom. The two olefinic π electrons are distributed over the two remaining rhodium atoms *via* a three-center delocalized μ-type bond. The empty sp^2 orbital on the second carbon atom of the olefin may be used as part of a three-center bonding MO involving an electron-pair coupling of the two equivalent rhodium atoms.

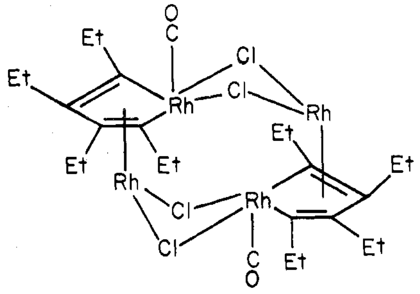


9

A second complex **5** was isolated by preparative tlc as a red solid from the same column band as **4**. It has not yet been fully characterized, but on the basis of elemental analysis it appears to have the composition $[(\pi\text{-}C_5H_5)Rh(PhC\equiv CPh)]_2$. The nmr spectrum of **5**, consisting of two π-C_5H_5 resonances at τ 4.50 and 5.08 (intensity 1:1), is in keeping with the proposed metallocyclic structure. Further, we have recently isolated the perfluorodiphenylacetylene derivative of this compound, **10a**, from a reaction between **1** and bis(pentafluorophenyl)acetylene.[14] The nmr spectrum of **10a** also exhibits two different π-C_5H_5 peaks (τ 4.67 and 5.53) in the ratio of 1:1. Professor L. F. Dahl at the University of Wisconsin has confirmed the structure of **10a** as that of a rhodacyclopentadiene ring π bonded to a second π-C_5H_5 unit.[23] Dickson has also isolated a similiar complex, **10b**, from a reaction between **1** and hexafluoro-2-butyne.[12] Such structures are analogous to that of the well-known iron complex, $Fe_2(CO)_6(C_4Ph_4)$.[20]



10a, R = Ph_f
10b, R = CF_3



11

A further basis for the proposed structure of **5** can be found in an examination of the literature of reactions of lower valent rhodium compounds with disubstituted acetylenes. Maitlis[24] has reported the formation of **11** as one of the products from a reaction between diethylacetylene and the chlororodicarbonylrhodium dimer. The structure, containing two rhodacyclopentadiene rings π bonded to two additional rhodium atoms, has been confirmed by a recent X-ray analysis.[25] Further, uncomplexed metallocyclopentadiene rings resulting from reactions of acetylenes with cobalt and rho-

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[21] Y. Iwashita and F. Tamura, *Bull. Chem. Soc. Jap.*, 43, 1517 (1970).

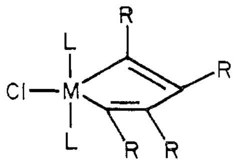
[22] J. Blount, L. F. Dahl, C. Hoogzand, and W. Hubel, *J. Amer. Chem. Soc.*, 88, 292 (1966).

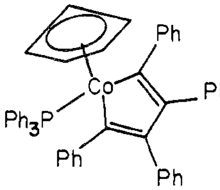
[23] L. F. Dahl, private communication.

[24] S. McVey and P. Maitlis, *J. Organometal. Chem.*, 19, 169 (1969).

[25] L. R. Bateman, P. M. Maitlis, and L. F. Dahl, *J. Amer. Chem. Soc.*, 91, 7292 (1969).

dium derivatives are known. Collman and coworkers[26] have proposed structure **12a** for a compound isolated in the course of their studies concerning the role of rhodium and iridium complexes in the catalytic cyclotrimerization of acetylenes, and Mague[27-29] has obtained complex **12b** from a reaction between hexafluoro-2-butyne and $Rh(SbPh_3)_3Cl$. The formation of the cobaltacyclopentadiene complex **13** from reactions of π-cyclopentadienyltriphenylphosphinecobalt diiodide, isopropylmagnesium bromide, and diphenylacetylene has also recently been reported.[30]





12a, M = Rh, Ir; L = PPh_3; R = CO_2Me, CO_2Et
b, M = Rh; L = $SbPh_3$; R = CF_3

13

The only data not completely consistent with this proposed structure for **5** is its mass spectrum. Although a small peak is observed at *m/e* 692 (parent ion), the major peak in the high mass region is that at *m/e* 680. This peak would correspond to the loss of 12 mass units and is presently unassignable. The mass spectrum does confirm, however, that **5** is a rhodium-containing species, showing large peaks at *m/e* 168 ($C_5H_5Rh^+$) and *m/e* 103 (Rh^+).

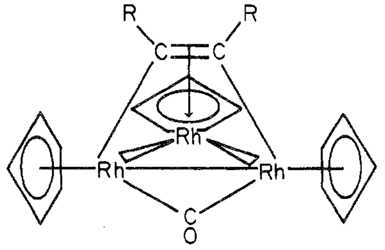
A third complex **6** was isolated from the reaction of **1** and **2** as dark green crystals and this product has not yet been fully characterized. The mass spectrum of **6** does indicate it to be a rhodium-containing compound since *m/e* 168 ($C_5H_5Rh^+$) and *m/e* 309 (Rh_3^+) are major peaks, although a parent ion for the complex is apparently not observed. This compound is currently being studied by X-ray diffraction methods in collaboration with Professor Dahl.

A fourth complex, carbonyldiphenylacetylenetris(π-cyclopentadienylrhodium) (**7**), has also been obtained from the reaction between **1** and **2**. Compound **7** was isolated as deep purple crystals which repeatedly gave poor analytical results. Thermal analytical studies indicated that the compound was in fact solvated by benzene even after extensive drying of the sample under vacuum at 50-55°.[31] Vacuum drying of this compound at 90° for 48 hr did remove this solvent of recrystallization, however, and excellent analytical results in agreement with the composition $(\pi\text{-}C_5H_5Rh)_3(CO)(PhC{\equiv}CPh)$ were then obtained. Only one $\pi\text{-}C_5H_5$ resonance (τ 4.80) was observed in the nmr spectrum of **7**, and its ir spectrum exhibited an extremely low carbonyl stretching frequency at 1675 cm^{-1}, indicating the presence of a doubly or triply bridging carbonyl ligand. The mass spectrum showed a parent ion peak at *m/e* 710 and a peak at *m/e* 682 corresponding to loss of CO. This transformation was supported by the presence of a metastable ion at *m/e* 655. A large peak at *m/e* 309 showing the presence of the Rh_3^+ ion was also observed. This complex is considered to be formally derived by replacement of the CO in the known[16-18] tris(π-cyclopentadienylcarbonylrhodium) isomers by **2**.

X-Ray structural studies on compound **7** have recently been completed by Dahl, and the structure is as shown above.[23] The best representation of bonding for **7**, which completely conforms to the experimental molecular parameters, arises from regarding **2** as an olefinic unit which is σ bonded to two of the rhodium atoms in the equilateral triangle *via* two sp^2-type orbitals. The remaining olefinic π electrons are then involved in a π-type bond with the unique rhodium. The carbonyl group is located on the opposite side of the rhodium triangle from the acetylene ligand and may be regarded as triply bridging. Preliminary results also indicate the presence of two molecules of benzene per unit cell of **7** in the crystalline state (each unit cell contains four molecules), thus confirming our previous findings.[31] The complex was commonly recrystallized from benzene-hexane mixtures and hence isolated as a solvate.

Several other papers have appeared in the literature concerning a related trinuclear rhodium compound.[32-34] Fischer[32] has reported the preparation of $(C_5H_5)_4Rh_3H$ from a reaction of $(C_5H_5)MgBr$ and $RhCl_3$. X-Ray structural studies[33-34] on this compound have confirmed the presence of a triangular $[(\pi\text{-}C_5H_5)Rh]_3$ unit with a fourth C_5H_5 unit bonded symmetrically to the array. Dickson has also isolated a compound similiar to **7**, $(\pi\text{-}C_5H_5Rh)_3(CO)(CF_3C{\equiv}CCF_3)$ (**14**).

Considering the structure of **7** in the solid state, the presence of only one $\pi\text{-}C_5H_5$ peak in the nmr spectrum is at first surprising. We have recently reported[14] on the isolation of **15**, the perfluorodiphenylacetylene analog of **7**, and have since this report been able to obtain a more reliable nmr spectrum of **15**. Complex **15** does in fact exhibit two different $\pi\text{-}C_5H_5$ peaks (τ 4.25 and 4.53) in the ratio of 1:2, and this result is consistent with the structure shown for **15** which was confirmed by Dahl.[23] The bonding of the acetylene ligand in **15** is analogous to that in **7**, and the only major difference in the structures is the presence of a doubly bridging carbonyl group in **15** (1810 cm^{-1}) rather than a triply bridging group as in **7**. Ideally then, the nmr spectrum of **7** should also exhibit two $\pi\text{-}C_5H_5$ peaks in the ratio of 1:2. This anomaly has recently been resolved by studies of Todd, *et al.*,[35] who have investigated the variable-temperature proton nmr spectrum of **7** and have verified the resolution of the cyclopentadienyl resonances in **7** into two distinct peaks (1:2 ratio) at approximately −80°.



14, R = CF_3
15, R = Ph_f

The final organorhodium product from reaction of **1** and **2** is represented by structure **8**, π-cyclopentadienyltetraphenylcyclopentadienonerhodium.[7] Complex **8** is a bright yellow solid which exhibits one $\pi\text{-}C_5H_5$ peak in its nmr spec-

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[26] J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, 7, 1298 (1968).
[27] J. T. Mague and G. Wilkinson, *Inorg. Chem.*, 7, 542 (1968).
[28] J. T. Mague, *J. Amer. Chem. Soc.*, 91, 3983 (1969).
[29] J. T. Mague, *Inorg. Chem.*, 9, 1610 (1970).
[30] H. Yamazaki and N. Hagihara, *J. Organometal. Chem.*, 21, 431 (1970).
[31] C. F. Meade, private communication.
[32] E. O. Fischer and H. Wawersik, *Chem. Ber.*, 101, 150 (1968).
[33] E. O. Fischer, O. S. Mills, E. F. Paulus, and H. Wawersik, *Chem. Commun.*, 643 (1967).
[34] O. S. Mills and E. F. Paulus, *J. Organometal. Chem.*, 11, 587 (1968).
[35] L. J. Todd, private communication.

trum (τ 4.69 d, $J_{\text{H-Rh}} = 1.0$ Hz). Such compounds are well known to be formed from the reactions of organorhodium compounds with acetylenes.[7,14]

The reaction of **1** and **2** in refluxing toluene has also been studied. This reaction yields compounds **3-8** in lesser yields than the reaction in refluxing xylene, in addition to a new product **16**. Complex **16** was isolated as a bright yellow solid with a composition (π-C_5H_5)Rh(PhC≡CPh)$_2C_7H_8$ as indicated by elemental analysis and mass spectrometry (M^+ 616). The loss of toluene from the molecule was evident by a major peak at *m/e* 524 in the mass spectrum of **16**, and this transformation was supported by a metastable peak at *m/e* 490. The toluene moiety appears to be chemically bound to the rhodium atom and not present simply as a solvate molecule, since **16** could be extensively dried at elevated temperature and at reduced pressure without affecting the toluene composition. The ir spectrum of **16** shows absorptions characteristic of aromatic and aliphatic C-H stretching frequencies and monosubstituted benzene rings, as well as methyl and π-cyclopentadienyl absorptions.

The nmr spectrum of **16** is shown in Figure 1. A resonance pattern and integration ratio consistent for four phenyl groups, one π-cyclopentadienyl ring, and one molecule of toluene are observed. The resonance pattern in the methyl region of the spectrum of **16** may possibly be due to the presence of several toluene-bound isomers. Maitlis, *et al.*,[36] have recently reported on the fluxional behavior of h^4-benzenerhodium and -iridium complexes. Fluxional character may also occur in **16**, and variable-temperature nmr studies to determine this point are currently in progress in collaboration with Professor Todd.[35]

The isolation of a complex such as **16** from a reaction between a π-cyclopentadienyldicarbonylmetal derivative and an acetylene in an aromatic solvent is of special importance in understanding the mechanism of formation of the many types of organorhodium complexes described above, since it indicates that the solvent may well play an integral role as a ligand in these processes. No coordinated arene complexes analogous to **16** could be isolated when the reaction between **1** and **2** was carried out in refluxing xylene. Presumably, under these more severe conditions, any such complexes formed are subsequently transformed into the other organorhodium complexes which were isolated. Attempts to detect analogous benzenerhodium complexes were not successful, since the use of refluxing benzene as solvent proved to be too mild, and no apparent reaction occurred between **1** and **2** even under prolonged reflux periods.

Because of a general interest in catalytic systems, including the cyclotrimerization of acetylenes using rhodium compounds,[21] an experiment was conducted to determine if **1** could catalytically trimerize **2** to **3**. Compounds **1** and **2** were caused to react in a molar ratio of 1:16 in refluxing xylene, and an 80% yield of hexaphenylbenzene **3** (based on **2**) was obtained. These results indicate the potential utility of **1** in catalytic reactions of this kind.

As an extension of our previous work involving reactions of **1** with bis(pentafluorophenyl)acetylene (**17**),[14] we have studied the reaction of π-cyclopentadienyldicarbonyliridium (**18**) with **17**. Preliminary runs were made, as in the case of rhodium, using refluxing xylene as the solvent. The Ir-CO bonds were not sufficiently labile at this temperature, however, and recovery of the starting materials resulted. Compounds **18** and **17** were subsequently caused to react at higher temperature in refluxing mesitylene for 72 hr. After cooling of the reaction to room temperature, as in the rhodium case,[14] a light yellow solid precipitated from solution and this was purified by vacuum sublimation at 185° (10^{-4} mm). The resulting white solid was identified as the cyclotrimerization product, hexakis(pentafluorophenyl)benzene (29%).

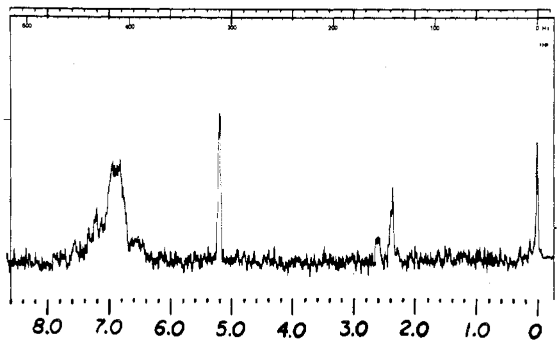
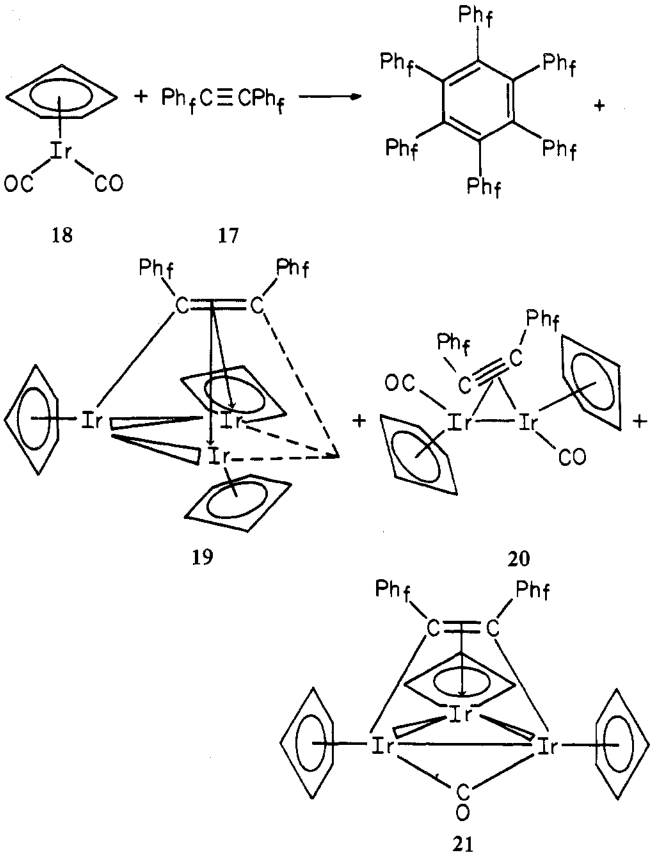


Figure 1. Nmr spectrum of complex **16**.



18

17

19

20

21

Chromatography of the dark reaction filtrate on an alumina column yielded the organoiridium products **19-21**. The first of these, complex **19**, was isolated as a yellow solid. Mass spectrometry identified the parent ion at *m/e* 1126-1132, indicating that three iridium atoms were present in each molecule (iridium has two isotopes: ^{191}Ir and ^{193}Ir). This parent ion corresponds to the structure (π-C_5H_5Ir)$_3$-(Ph$_f$C≡CPh$_f$) (**19**) as illustrated above. The compound can thus be formulated as the iridium analog of complex **4**, with substitution of bis(pentafluorophenyl)acetylene for **2** in the molecule. Like **4**, complex **19** contains only one π-C_5H_5 resonance in its nmr spectrum (τ 5.03) and may be fluxional in solution. The ir spectrum of **19** confirmed the absence of terminal or bridging carbonyl groups.

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[36] J. W. Kang, R. F. Childs, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **92**, 720 (1970).

Elemental analysis and mass spectrometry (*m/e* 926-930, two iridium atoms) have resulted in identification of the second organoiridium compound from the reaction of **17** and **18** as complex **20**. Since both CO ligands are terminal (1970 cm^{-1}) as evidenced by the ir spectrum of **20**, it is possible that an Ir-Ir bond does occur in this compound. Unfortunately, suitable crystals for X-ray structural analysis have not yet been obtained, and the exact structure of **20** is still unknown. Dickson has reported the formation of a similiar complex, $(\pi\text{-}C_5H_5)_2Rh_2(CO)_2(CF_3C{\equiv}CCF_3)$, from a reaction of **1** and hexafluoro-2-butyne[12] and has discussed the possibility of its intermediacy in the cyclization of acetylenes by **1**. Our isolation of **20** in the iridium series tends to substantiate this conclusion.

The final organoiridium complex obtained from the reaction of **17** and **18** is illustrated by structure **21**, bis(pentafluorophenyl)acetylenecarbonyltris(π-cyclopentadienyliridium). This complex is formally the iridium analog of compound **15**. Like **15**, complex **21** exhibits a very low CO stretching frequency (1760 cm^{-1}) and shows two $\pi\text{-}C_5H_5$ peaks (τ 4.62 and 4.75, ratio 1:2) in its spectrum. The parent ion (1154-1160, three iridium atoms) also exhibits peaks for the loss of CO in the mass spectrometer.

A reaction of **17** and **18** for only 24 hr in refluxing mesitylene resulted in lower yields of hexakis(pentafluorophenyl)benzene and complex **21**, as well as formation of a small amount of a new product **22**, which has the apparent composition $(\pi\text{-}C_5H_5Ir)_2(Ph_fC{\equiv}CPh_f)_2(CO)$. A parent ion (1256-1260, two iridium atoms) for this complex is noted in its mass spectrum, in addition to a group of peaks at 1228-1232, corresponding to loss of CO. The ir spectrum also exhibits a strong CO frequency in the terminal region at 2040 and 1970 cm^{-1}. Unfortunately, this product is as yet not fully characterized due to difficulty in obtaining sufficient amounts of a pure sample.

Reactions of **18** with **2** were attempted in refluxing xylene; however no identifiable products were obtained under these reaction conditions.

The iridium complex **18** is thus observed to react with disubstituted acetylenes in a manner somewhat similiar to that of the rhodium compound **1**. Additional studies are currently in progress in order to determine the extent of this similarity and to elucidate further the mechanistic pathways by which these many organorhodium and -iridium complexes are formed.

Experimental Section

All operations, including column chromatography, were carried out under a nitrogen atmosphere using Schlenk-tube techniques. Hexane, benzene, toluene, xylene, and mesitylene were purified by distillation from calcium hydride under nitrogen. Ethyl ether was predried over calcium chloride and then distilled from sodium-benzophenone. Diphenylacetylene[37] and bis(pentafluorophenyl)acetylene[38] were prepared using published procedures. π-Cyclopentadienyldicarbonylrhodium (1) was prepared in *ca.* 85% yield from a reaction between excess freshly sublimed thallium cyclopentadienide and $[Rh(CO)_2Cl]_2$ in hexane. π-Cyclopentadienyldicarbonyliridium (18) was prepared in *ca.* 80% yield by reaction of chlorotricarbonyliridium (Strem Chemicals, Inc.) and freshly sublimed thallium cyclopentadienide in hexane. CAMAG neutral-grade alumina was used for column chromatography and was deactivated with 5% water and stored under nitrogen before use. CAMAG silica gel was used for preparative tlc; the plates were 20 × 20 cm and had an absorbent thickness of 1.2 mm. Microanalyses were preformed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts. Mass spectra were recorded on a AEI MS-9 mass spectrometer using the direct-inlet system, at a source temperature of *ca.* 250°.

Reaction of π-Cyclopentadienyldicarbonylrhodium (1) and Diphenylacetylene (2) in Xylene. Diphenylacetylene (**2**) (6.36 g, 35.7 mmol) and π-cyclopentadienyldicarbonylrhodium (**1**) (4.0 g, 17.8 mmol) were mixed with 50 ml of dry xylene in a flask which had previously been flamed out under vacuum and flushed with nitrogen. The reaction flask was covered with aluminum foil in order to minimize exposure to the light, and the contents were heated at reflux for 24 hr. After cooling to room temperature, the black reaction mixture was filtered to remove a white solid which was identified as hexaphenylbenzene (**3**) (3.5 g, 55%), mp 454° (lit.[3] mp 454–455°).

The black filtrate was chromatographed under nitrogen on an alumina column (2.5 × 35 cm) which had been packed in hexane. Elution with hexane brought down the two starting materials (evidenced by tlc) as an orange band. An increase in polarity to 75% benzene in hexane resulted in elution of a second orange band, shown by tlc to consist of two major components. This band was evaporated to dryness, dissolved in a minimum amount of benzene, and placed on preparative tlc plates (50 mg/plate). One elution with 25% benzene in hexane moved the first orange band *ca.* three-fourths of the way up the plate. The orange band was scraped from the plates, extracted with ethyl ether, and filtered. The resulting red filtrate was evaporated to dryness and the product was recrystallized from benzene–hexane to yield 0.025 g of 4 (0.6%) as an orange-red solid. *Anal.* Calcd for $C_{29}H_{25}Rh_3$: C, 51.06; H, 3.70. Found: C, 51.30; H, 3.82. The molecular weight of 4 is 682 as determined by mass spectrometry (calcd 682). An ir spectrum (KBr) showed the following major peaks: 1600 (m), 1495 (m), 1440 (m), 1030 (w), 790 (m), 695 (s) cm^{-1}. The nmr spectrum ($CDCl_3$) exhibited a singlet at τ 4.96 ($\pi\text{-}C_5H_5$) and a multiplet in the region τ 2.2–3.0 ($-C_6H_5$).

The preparative tlc plates were then eluted once with benzene to move the second red band *ca.* 2 cm up from the origin. This band was scraped from the plates, extracted with ethyl ether, and filtered, yielding 0.045 g of a deep red solid **5** (0.7%). An analytical sample was prepared by recrystallization from benzene–hexane. *Anal.* Calcd for $C_{38}H_{30}Rh_2$: C, 65.91; H, 4.37. Found: C, 65.75; H, 4.47. The following peaks were observed in the mass spectrum: 692 (molecular ion), 680, 632, 604, 534, 511, 435, 309, 270, 233, 168, 142, 103. An ir spectrum (KBr) of **5** exhibited the following major peaks: 1680 (m), 1600 (m), 1490 (m), 1445 (m), 1400 (w), 1340 (m), 1260–1240 (m), 1100 (m), 1070 (m), 1020 (m), 795 (s), 695 (s) cm^{-1}. The nmr spectrum ($CDCl_3$) showed two singlets at τ 4.50 and 5.08 ($\pi\text{-}C_5H_5$, relative intensity 1:1) and a multiplet at τ 2.7–3.5 ($-C_6H_5$, relative intensity 2).

Following the second orange band from the column was a large purple band which was eluted with 25% ether in benzene. Tlc indicated that this band consisted of a major purple product mixed with a small amount of green contaminant. After evaporation to dryness, the dark solid was taken up in a minimal amount of benzene and rechromatographed on an alumina column (2.5 × 35 cm) which had been packed in hexane. Elution with benzene brought the green component down first as a separate band. Further elution with benzene removed the purple band from the column.

The green band was evaporated to dryness and recrystallized from benzene–hexane, producing 0.010 g of a dark green solid (**6**). The following peaks were observed in the mass spectrum: 386, 309, 267, 178, 168. An ir spectrum (KBr) of 6 exhibited the following peaks: 1850 (m), 1800 (m), 1700 (s), 1600 (w), 1495 (m), 1445 (m), 1400 (w), 1350 (m), 1150 (w), 795 (w), 750 (m), 695 (s) cm^{-1}.

The purple band was evaporated to dryness and the resulting solid was recrystallized twice from benzene–hexane, yielding 0.18 g (4.3%) of carbonyldiphenylacetylenetris(π-cyclopentadienylrhodium) (7) as a dark purple solid. An analytical sample was prepared by drying this sample at 90° (0.01 mm) for 48 hr. *Anal.* Calcd for $C_{30}H_{25}ORh_3$: C, 50.73; H, 3.55; O, 2.25; Rh, 43.47. Found: C, 50.92; H, 3.47; O, 2.30; Rh, 43.45. The molecular weight of 7 is 712 as determined by osmometry in benzene at 50° and 710 as determined by mass spectrometry (calcd 710). An ir spectrum (KBr) exhibited the following bands: 3140–2960 (m), 1855 (m), 1800 (m), 1675 (vs), 1590 (m), 1490 (m), 1100 (m), 995 (m), 900 (m), 830–635 (m) cm^{-1}. The nmr spectrum ($CDCl_3$) consisted of a singlet at τ 4.80 ($\pi\text{-}C_5H_5$, relative intensity 3) and a multiplet at τ 2.5–3.2 ($-C_6H_5$, relative intensity 2).

A fourth band (yellow) was eluted from the original column using ethyl ether. This band was evaporated to dryness, yielding 2.0 g (21%) of a yellow solid identified as π-cyclopentadienyltetraphenylcyclopentadienonerhodium (8), mp 334–336°. Recrystallization of the product from chloroform–hexane produced an analytical sample

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of the same melting point. *Anal.* Calcd for $C_{34}H_{25}ORh$: C, 73.91; H, 4.56; O, 2.90; Rh, 18.63. Found: C, 73.90; H, 4.57; O, 2.82; Rh, 18.65. The molecular weight was 552 as determined by mass spectrometry (calcd 552). An ir spectrum (KBr) exhibited the following major bands: 3060 (m), 1605 (s), 1595 (s), 1570 (m), 1500 (m), 1065 (m), 1020 (m), 740 (s), 690 (s) cm^{-1}. The nmr spectrum ($CDCl_3$) consisted of a doublet at τ 4.69 (π-C_5H_5, relative intensity 1, $J_{H\text{-}Rh}$ = 1.0 Hz) and two multiplets at τ 2.73–2.99 and 2.36–2.53 (–C_6H_5, relative intensity 4).

Reaction of π-Cyclopentadienyldicarbonylrhodium (1) and Diphenylacetylene (2) in Toluene. The reaction was carried out as described above for the same reaction in xylene, except that refluxing toluene was used as the solvent. An analogous work-up of the reaction produced the following products: hexaphenylbenzene (**3**) (3.0 g, 47%), **4** (0.010 g), **5** (0.005 g), **6** (0.005 g), carbonyldiphenylacetylenetris(π-cyclopentadienylrhodium) (**7**) (0.110 g), π-cyclopentadienyltetraphenylcyclopentadienonerhodium (**8**) (1.9 g, 19%), and a new product **16**.

Complex **16** was isolated from the first orange band eluted from the column with hexane. Tlc indicated that this band contained amounts of a yellow compound in addition to the two starting materials **1** and **2**. The solution was evaporated to dryness and the residue was triturated with hot pentane, leaving a yellow solid. This solid was dissolved in a minimum amount of benzene and placed on preparative tlc plates (50 mg/plate). One elution with 1:1 benzene–hexane separated the remaining starting materials from the major yellow band. This band was scraped from the plates, extracted with ethyl ether, filtered, and evaporated to dryness. Recrystallization of the residue from benzene–hexane yielded 0.15 g (1.4%) of a yellow solid (**16**), mp 205–207°. *Anal.* Calcd for $C_{40}H_{33}Rh$: C, 77.92; H, 5.39; Rh, 16.69. Found: C, 77.88; H, 5.39; Rh, 16.73. The molecular weight was 616 as determined by mass spectrometry (calcd 616). An ir spectrum (KBr) exhibited the following major bands: 3110–2810 (w), 1595 (m), 1490 (m), 1440 (m), 1255 (s), 1180–965 (s), 790 (s), 685 (s) cm^{-1}. The nmr spectrum ($CDCl_3$) consisted of a doublet at τ 4.79 (π-C_5H_5, relative intensity 5, $J_{H\text{-}Rh}$ = 1.0 Hz), a multiplet at τ 2.3–3.6 (–C_6H_5, relative intensity 25), and two multiplets at τ 7.40 and 7.65 (–CH_3, relative intensity 3).

Reaction of π-Cyclopentadienyldicarbonylrhodium (1) and Excess Diphenylacetylene (2). Diphenylacetylene (**2**) (3.0 g, 16.8 mmol) was dissolved in 25 ml of xylene in a flask which had been flamed out under vacuum and flushed with nitrogen. π-Cyclopentadienyldicarbonylrhodium (**1**) (0.25 g, 1.11 mmol) was mixed with 20 ml of xylene and placed in the reaction flask. The flask was covered with aluminum foil in order to minimize exposure to the light, and the contents were heated at reflux for 23 hr. After cooling to room temperature, the reaction mixture was filtered to remove 2.41 g of hexaphenylbenzene (**3**) (80.5% based on diphenylacetylene) which had precipitated, mp 454° (lit.[3] mp 454–455°).

Tlc of the black filtrate indicated that the other expected products **3–8** were formed, but no attempt was made to isolate them.

Reaction of π-Cyclopentadienyldicarbonyliridium (18) and Bis(pentafluorophenyl)acetylene (17). This reaction was run twice, using two different reaction times: method A (72 hr) and method B (24 hr).

Method A. Bis(pentafluorophenyl)acetylene (17) (3.75 g, 10.5 mmol) and π-cyclopentadienyldicarbonyliridium (**18**) (1.6 g, 5.1 mmol) were mixed with 50 ml of mesitylene in a flask which had previously been flamed out under vacuum and flushed with nitrogen. The reaction flask was covered with aluminum foil in order to minimize exposure to the light and the contents were heated at reflux for 72 hr. After cooling to room temperature, filtration of the reaction mixture yielded a tan solid which was washed well with hexane and purified by vacuum sublimation at 185° (10^{-4} mm). The resulting white solid (1.1 g, 29%) was identified as hexakis(pentafluorophenyl)benzene[14] by mass spectrometry and elemental analysis.

The dark filtrate was chromatographed under nitrogen on an alumina column (2.5 × 35 cm) which had been packed in hexane. Elution with hexane removed a yellow band from the column which contained two yellow products and a large amount of starting materials. The yellow solution was evaporated to dryness, and vacuum sublimation at 85° (10^{-4} mm) removed 2.3 g (61% recovery) of unreacted **17**. The yellow residue remaining in the sublimer was dissolved in a minimal amount of benzene and placed on preparative tlc plates (50 mg/plate). One elution with 25% benzene in hexane separated the two yellow compounds from the remaining starting materials, and each band was scraped from the plates, extracted with ethyl ether, and filtered.

The top yellow band from the plates was evaporated to dryness and recrystallized from ether–hexane, yielding 0.010 g (0.5%) of bis(pentafluorophenyl)acetylenetris(π-cyclopentadienyliridium) (19) as yellow crystals, mp 280–282°. The molecular weight was 1126–1132 as determined by mass spectrometry (calcd 1126–1132). An ir spectrum (KBr) exhibited the following major bands: 1510 (s), 1470 (s), 1155 (w), 1100 (w), 1030 (m), 985 (m), 820 (s), 725 (m), 675 (w) cm^{-1}. The nmr spectrum ($CDCl_3$) consisted of a singlet at τ 5.03 (π-C_5H_5).

The bottom yellow band from the plates was evaporated to dryness and recrystallized from ether–hexane, yielding a yellow solid (0.020 g, 0.85%) identified as μ-bis(pentafluorophenyl)acetylene-bis(π-cyclopentadienylcarbonyliridium) (20), mp 238–240°. *Anal.* Calcd for $C_{26}H_{10}F_{10}Ir_2O$: C, 33.62; H, 1.08; F, 20.46; Ir, 41.39; O, 3.44. Found: C, 33.12; H, 1.54; F, 20.36; Ir, 41.29; O, 3.40. The molecular weight was 926–930 as determined by mass spectrometry (calcd 926–930). An ir spectrum (KBr) exhibited the following bands: 1970 (vs), 1610 (m), 1510–1480 (s), 1290 (w), 1105 (m), 980 (s), 825 (s), 710 (w), 670 (m), 640 (m) cm^{-1}.

Benzene elution removed a second band (red) from the column. The red solution was evaporated to dryness, dissolved in a small amount of benzene, and placed on preparative tlc plates (50 mg/plate). Elution of the plates with benzene separated the major red band from several minor impurities. This band was scraped from the plates, extracted with ethyl ether, filtered, and evaporated to dryness. The product was recrystallized from benzene–hexane, yielding 0.010 g (0.5%) of carbonylbis(pentafluorophenyl)acetylenetris(π-cyclopentadienyliridium) (**21**) as a red solid. The molecular weight was 1154–1160 as determined by mass spectrometry (calcd 1154–1160). An ir spectrum (KBr) exhibited the following major bands: 1760 (s), 1510 (s), 1480 (s), 1400 (w), 1255 (w), 1090 (m), 980 (m), 820–800 (m), 660 (w) cm^{-1}. The nmr spectrum ($CDCl_3$) consisted of two singlets (relative intensity 1:2) at τ 4.62 and 4.75.

Method B. Bis(pentafluorophenyl)acetylene (**17**) (5.0 g, 14 mmol) and π-cyclopentadienyldicarbonyliridium (**18**) (2.15 g, 7 mmol) were mixed with 50 ml of mesitylene in a flask which had previously been flamed out under vacuum and flushed with nitrogen. The flask was covered with aluminum foil in order to minimize exposure to the light and the contents were heated at reflux for 24 hr. After cooling to room temperature, filtration of the reaction mixture yielded 0.30 g (6%) of a white solid identified as hexakis(pentafluorophenyl)benzene.[14] Purification was achieved by vacuum sublimation at 185° (10^{-4} mm).

The filtrate was chromatographed under nitrogen on an alumina column (2.5 × 35 cm) which had been packed in hexane. Elution with hexane removed a yellow band which was evaporated to dryness and subjected to vacuum sublimation at 85° (10^{-4} mm) in order to remove 4.3 g (86% recovery) of starting **17**. The solid remaining in the sublimer was dissolved in a small amount of benzene and placed on preparative tlc plates (50 mg/plate). Elution with 1:1 benzene–hexane separated the major yellow band from the remaining starting materials, and this band was removed from the plates, extracted with ethyl ether, and filtered. Evaporation to dryness yielded 0.012 g (0.27%) of crude **22** as a yellow-brown solid. The mass spectrum of **22** exhibited peaks at 1256–1260 (molecular ion) and 1228–1232 (loss of CO) where the molecular ion is $C_{39}H_{10}F_{20}Ir_2O$. An ir spectrum (KBr) contained the following bands: 2040–1970 (s), 1645 (w), 1500 (s), 1100–1085 (m), 980 (s), 830 (w), 640 (w) cm^{-1}. An nmr spectrum of the crude product ($CDCl_3$) exhibited one broad signal at τ 4.49 (π-C_5H_5).

Further elution of the original column with benzene removed a small red band. The red solution was evaporated to dryness, dissolved in a minimal amount of benzene, and placed on preparative tlc plates (50 mg/plate). One elution with benzene separated the major red band from several minor impurities. This band was scraped from the plates, extracted with ethyl ether, filtered, and evaporated to dryness. The resulting red solid weighed 0.005 g (0.19%) and was identified as carbonylbis(pentafluorophenyl)acetylenetris(π-cyclopentadienyliridium) (**21**).

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Electrostatic Effects in Coordination Kinetics. Reaction of Nickel(II) Ion with a Cationic Unidentate Ligand as a Function of Solvent Dielectric

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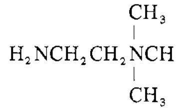
The kinetics of solvated Ni(II) ion reacting with a cationic ligand, *N,N,N*-trimethylethylenediammonium ion ($tmen^+$), have been studied as a function of solvent dielectric in methanol–water mixtures containing 0–90% methanol (by weight) at 25°, $\mu = 0.3\ M$ using the temperature-jump relaxation technique. By comparison of the experimental formation rate constants to the corresponding values for Ni(II) reacting with the neutral ammonia ligand, the value of the charge center-to-center distance between Ni(II) and $tmen^+$ in the "effective" ion pairs leading to complex formation is found to be 6.5 Å. In conjunction with a previously generated value for the reactive site center-to-center distance of 4 Å along with estimated steric factors, this value permits the calculation of a "reactive" ion-pair formation constant for charged bidentate ligands interacting with metal ions. The validity of the calculations in the current treatment is limited by the relatively high ionic strength necessitated in this study. The mechanistic implications for coordination reactions involving amino acids and monoprotonated diamines are considered.

Introduction

In recent reports emanating from this laboratory, we have attempted to quantify fundamental steric[1-3] and solvent[4-7] effects upon the kinetics of coordination reactions involving hexacoordinated transition metal ions in solution. For uncharged ligands, analysis of the data in terms of a dissociative mechanism has been reasonably straightforward. However, for charged multidentate ligands, such as the protonated polyamines,[2,3,6] the resolution of steric and solvent effects has been hampered by a lack of specific quantitative information on the magnitude of the accompanying electrostatic effects.

We now wish to report the results of a study in which we have attempted to establish the actual magnitude of such electrostatic interactions. For this purpose we have chosen to examine the kinetics of solvated Ni(II) ion reacting with a cationic unidentate ligand, *N,N,N*-trimethylethylenediammonium ion ($tmen^+$).



$$H_2NCH_2CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}}CH_3^+$$

This ligand has been selected to serve as a model for singly charged bidentate ligands in which the charged site is located at the donor atom *not* involved in first-bond formation (*e.g.*, monoprotonated ethylenediamine, glycinate, etc.).

The kinetics of the Ni–tmen reaction have been studied as a function of solvent dielectric in methanol–water mixtures. By making the reasonable assumption that steric effects associated with $tmen^+$ will remain constant in all solvent compositions, a comparison of the resolved formation rate constants with corresponding values generated previously for the reaction between Ni(II) and NH_3 in the same solvent mixtures[4] allows us to isolate the electrostatic effects in the current system.

In analyzing the data, we have made a distinction between two distance parameters in the ion pairs leading to complex formation: (i) the center-to-center distance of closest approach between the solvated metal ion and the *reactive site* on the ligand, and (ii) the accompanying center-to-center distance between the solvated metal ion and the *charged site* on the ligand. Such a distinction, which appears to have been ignored by previous investigators, derives from the concept of a *reactive* outer-sphere complex in which the ligand must be properly oriented relative to the metal ion at the time of metal–solvent bond rupture in order to compete for the vacated coordination site. This concept is in accord with the hypothesis that a dissociative interchange (I_d) mechanism is operative in such ligand substitution reactions.

The use of a cationic rather than an anionic ligand in this work yields two definite advantages: (i) the possibility of extensive ion-pair formation in low dielectric media is eliminated, and (ii) the distinction between the two distance parameters is enhanced. The values generated for these two parameters are subsequently applied to an analysis of experimental rate constants which have been reported in the literature for reactions involving monoprotonated diamines and amino acids.

Experimental Section

Reagents. $Ni(NO_3)_2 \cdot 6H_2O$ (Baker "Analyzed Reagent") was used as the source of nickel ion in aqueous solution while $Ni(ClO_4)_2$ was used for all other solvent mixtures, the preparation, purification, and standardization procedures for the latter having been previously described.[4] The ligand salt, tmen·Br·HCl, was synthesized from 2-bromoethylphthalimide and trimethylamine as described in the literature[8,9] with the following modifications in purification. The final solution, resulting from heating the intermediate trimethyl-2-phthal-

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