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(12) In *refluxing* tetraglyme both methyl iodide and acetic anhydride also served to induce fragmentation of **4** to **6**.

(13) Diol (**2**) was also isolated from the pyrolysis reaction in 20–30% yield. The origin of the diol is not clear. Although we took great pains to thoroughly dry the tetraglyme used, we cannot rule out small amounts of adventitious water in the solvent as being responsible, at least in part, for the formation of the diol. The yield of **2** was smallest when **4** and 1 equiv of acetic acid were pyrolyzed in the absence of solvent.

(14) The dimer proved so insoluble that 1.5×10^5 pulses had to be accumulated in order to obtain a satisfactory ^{13}C spectrum from a supersaturated $CDCl_3$ solution.

(15) The parent [3.3.2]propellane has been prepared: W. T. Borden, I. L. Reich, L. A. Sharpe, R. B. Weinberg, and H. J. Reich, *J. Org. Chem.*, **40**, 2438 (1975).

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(18) All other molecular parameters agree well with generally anticipated values. Details can be found in the supplementary material.

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(21) Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Awardee, 1972–1977.

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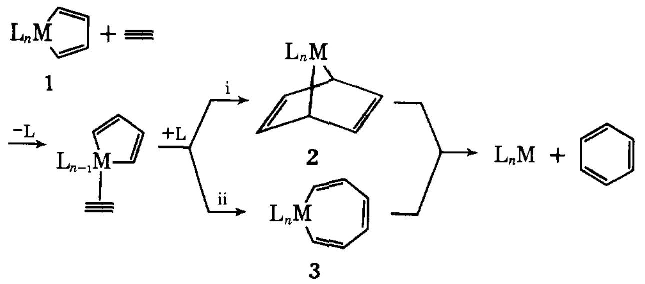
Parallel Reaction Pathways in the Cobalt-Catalyzed Cyclotrimerization of Acetylenes

Sir:

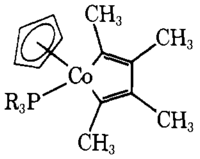
A variety of transition metal compounds catalyzes the cyclotrimerization of alkynes to arenes.[1-3] In many cases, particularly with low valent metal catalysts, metalocyclopentadienes or metalloles (**1**, cf. Scheme I), formed by oxidative cyclization of two coordinated alkynes, have been implicated as intermediates in the catalytic cycle.[4]

Two modes of reaction of alkynes with metalloles have been suggested (Scheme I): (i) Diels–Alder addition of a coordinated alkyne to the diene moiety of the metallole generating bicyclic intermediate (**2**) and (ii) insertion of a coordinated acetylene into a metal-carbon σ bond leading to metalocycloheptatriene (**3**). In either case the final step is reductive elimination of arene with release of the coordinatively unsaturated metal fragment, It has been tacitly assumed that coordination of the alkyne precedes either i or ii. Indeed, Collman and co-workers report that blocking the vacant coordination site of $IrCl(PPh_3)_2\{C_4(CO_2Me)_4\}$ with CO inhibits completely the cyclotrimerization of dimethylacetylene dicarboxylate by this metallole.[4a]

Scheme I



As part of an investigation of alkyne cyclotrimerization catalyzed by phosphine derivatives of (η^5-cyclopentadienyl)cobalt, we have examined the reactions of alkynes with trialkyl- and triarylphosphinecyclopentadienylcobalta-2,3,4,5-tetramethylcyclopentadiene (**4**). We find that the mechanism of the reaction is critically dependent upon the nature of the alkyne.



4a, $R = C_6H_5$
b, $R = C_2H_5$
c, $R = CH_3$

The reaction of $(\eta^5\text{-}C_5H_5)Co(PPh_3)_2$ (**5**) with 2 equiv of 2-butyne (**6**) in refluxing benzene affords yellow-brown **4a** rapidly and in good yield.[5] In a sealed tube in benzene at 120 °C, **4a** catalyzes the trimerization of **6** to hexamethylbenzene (**7**);[6] this process may be monitored conveniently by NMR spectrometry. In the presence of excess triphenylphosphine, the pseudo-first-order rate fits the expression:

$$\frac{d[\mathbf{7}]}{dt} = k_{\text{obsd}} \frac{[\mathbf{4a}][\mathbf{6}]}{[PPh_3]}$$

This rate law is consistent with the mechanism outlined in Scheme II, involving substitution of PPh_3 by **6** via coordinatively unsaturated intermediate **8.** Assuming this mechanism,

$$\text{rate} = \frac{d[\mathbf{7}]}{dt} = \frac{k_1 k_3 [\mathbf{4a}][\mathbf{6}]}{k_{-1}[PPh_3] + k_3[\mathbf{6}]}$$

so at high $[PPh_3]$ where $k_{-1}[PPh_3] \gg k_3[\mathbf{6}]$,

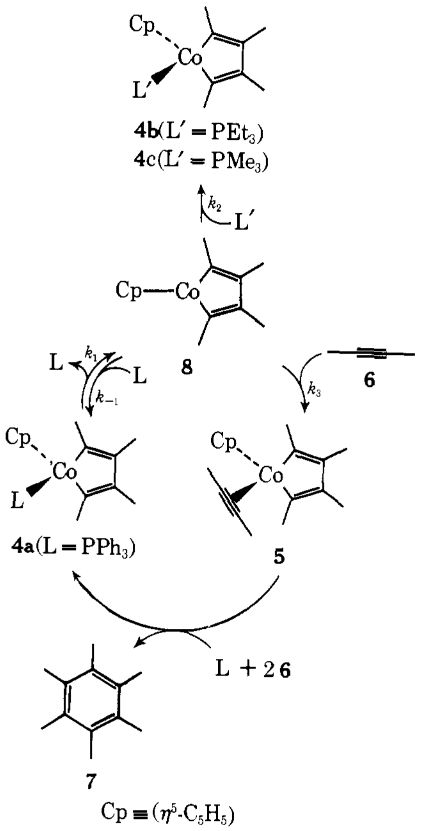
$$k_{\text{obsd}} = \frac{k_1 k_3}{k_{-1}} = 4.5 \times 10^{-5}\ s^{-1}$$

This mechanism is also supported by kinetic data under conditions of high acetylene and low phosphine concentrations. If under these conditions $k_3[\mathbf{6}] \gg k_{-1}[PPh_3]$, the rate law reduces to

$$\frac{d[\mathbf{7}]}{dt} = k_1[\mathbf{4a}]$$

Since the concentration of catalyst does not change, an overall zero-order rate is expected.[7] Accordingly, the rate of appearance of hexamethylbenzene at 74 °C in a benzene solution initially containing 1.90 M **6** and 0.19 M **4a** was followed by ^1H NMR spectrometry and found constant (2.0×10^{-5} M s^{-1})

Scheme II



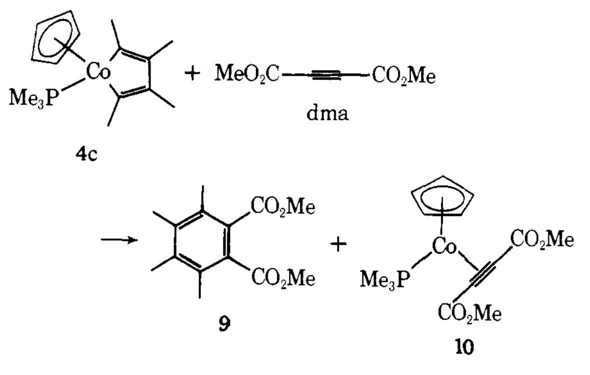
for at least five turnovers of **4a**. The first-order rate constant (k_1) for dissociation of triphenylphosphine from **4a** is thus $1.1 \times 10^{-4}\ s^{-1}$.

Trialkylphosphines such as triethylphosphine and trimethylphosphine quantitatively displace triphenylphosphine from **4a** to yield **4b** and **4c**, respectively.[8] The rate of conversion of **4a** to **4b** at 74 °C, again monitored by ^{1}H NMR spectrometry, is found to be first order in **4a** ($k_{obsd} = 5.8 \times 10^{-5}\ s^{-1}$) but independent of the concentration of triethylphosphine. Furthermore, the rate is unchanged by addition of as much as a five molar excess of triphenylphosphine. These kinetic data are also consistent with a mechanism involving initial dissociation of triphenylphosphine from **4a** (Scheme II). The rapid rate at which trialkylphosphines scavenge **8** once again dictates a rate law zero order in entering ligand. The value of k_1 measured in this way ($5.8 \times 10^{-5}\ s^{-1}$) is in reasonable agreement with that obtained from the kinetics of the trimerization of **6** ($1.1 \times 10^{-4}\ s^{-1}$), considering the fact that the reaction medium is substantially different in the two cases.[9]

The reaction of these metalloles with dimethylacetylene dicarboxylate (dma) operates in a strikingly different way. The high affinity of triethylphosphine or trimethylphosphine for the formal Co(III) center of **8** prevents ready dissociation of these ligands from **4b** and **4c**. For example, no reaction is observed for **4c** and **6** at 75 °C and even after several days at 120 °C very little hexamethylbenzene can be detected. Dimethylacetylene dicarboxylate, on the other hand, reacts with **4c** cleanly and stoichiometrically (eq 1) *at room temperature*, affording the expected arene, 3,4,5,6-tetramethylphthalate dimethyl ester (**9**).[10] (η^5-C$_5$H$_5$)Co(PMe$_3$)(dma) (**10**) was isolated by chromatography on deactivated alumina and identified by its NMR spectrum.[11] The kinetics of this reaction were monitored both by ^{1}H NMR spectrometry and by visible spectrophotometry. In the presence of excess dma[12] the pseudo-first-order rate fits the expression:

$$-\frac{d[\mathbf{4c}]}{dt} = \frac{d[\mathbf{10}]}{dt} = k_4[\mathbf{4c}][\text{dma}]$$

where the value of the second-order rate constant (k_4) at 24 °C is $2.7 \times 10^{-3}\ M^{-1}\ s^{-1}$. These results clearly indicate that the reaction of **4c** with dma proceeds readily without prior dissociation of its phosphine ligand, in direct contrast to the behavior of such metalloles with 2-butyne.



(1)

One mechanism consistent with these observations involves a rate-determining direct Diels–Alder addition of dma to the diene moiety of the metallocycle.[13] The Diels–Alder product (cf. 2, Scheme I) may be expected to reductively eliminate arene (**9**) releasing coordinatively unsaturated (η^5-C$_5$H$_5$) Co(PMe$_3$) which in the presence of excess dma generates **10.** But whatever the exact mechanism of the reaction of **4c** with dma, it is clear that not only is substitution of phosphine by alkyne not rate determining (as is the case in the reaction of 2-butyne with **4a**), in fact trimethylphosphine dissociation is not part of the mechanism at all.[12]

We conclude that there exist at least two distinct mechanisms for the production of arenes from the reaction of alkynes with metalloles such as **4.** One path involves entry of alkyne into the coordination sphere of the metal; the other is characterized by direct reaction of uncomplexed alkyne with the metallole. The latter pathway is observed between an electron-rich diene moiety and an electron-poor, powerfully dienophilic alkyne, suggesting a Diels–Alder process.

Acknowledgment. This work has been supported by the National Science Foundation (Grant Nos. MPS 75-03056 (JEB) and CHE-74-14711 (RGB)), to whom grateful acknowledgment is made.

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(5) **4a** is isolated by column chromatography on deactivated alumina and recrystallized from benzene–pentane. ^{1}H NMR (benzene-d_6): (η^5-C$_5$$H_5$) s, δ 4.73 (5 H); [C$_4$(C$H_3$)$_4$] s, 2.23 (6 H) and s, δ 1.60 (6 H); P(C$_6$H$_5$)$_3$ multiplet δ 6.8–7.7. Calcd for C$_{31}$H$_{32}$PCo: C, 75.29; H, 6.53; Co, 11.93. Found C, 75.03; H 6.47; Co, 11.87.

(6) Identified by ^{1}H NMR (benzene-d_6): S= Δ 2/[2/

(7) An overall zero-order reaction rate requires regeneration of **4a** following release of **7,** rather than some alternative cycle involving only **5, 6, 7,** and **8.** These implications will be addressed more fully in a forthcoming full paper.

(8) **4c** was isolated by column chromatography on deactivated alumina and recrystallized from benzene–pentane. ^{1}H NMR (benzene-d_6): (η^5-C$_5$$H_5$) s, δ 4.52 (5 H); [C$_4$(C$H_4$)$_4$] s, δ 2.27 (6 H) and s, δ 1.92 (6 H); –P(CH_3)$_3$ d($^2J_{^{31}P-^1H}$ = 10 Hz), δ 0.80 (9 H). **4b** was not isolated but identified by ^{1}H NMR (benzene-d_6): (η^5-C$_5$$H_5$) s, δ 4.53 (5 H); [C$_4$(C$H_4$)$_4$] s, δ 2.40 (6 H), and s, δ 2.00 (6 H); –P(C$_2$$H_5$)$_3$ multiplet, δ 0.6–1.3.

(9) The compositions of the two solutions (by weight) are: (a) 34% P(C$_2$H$_5$)$_3$, 66% C$_6$D$_6$; (b) 11% **6,** 89% C$_6$D$_6$.

(10) (a) **9** was isolated by column chromatography on deactivated alumina. ^{1}H

NMR (benzene-d_6): s, δ 3.53 (6 H); s, δ 2.15 (6 H); s, δ 1.77 (6 H). Melting point 127–128 °C; reported 127 °C, R. Criegee and F. Zanker, *Angew. Chem.*, **76**, 716 (1964); (b) **4a** reacts with dma at a rate comparable to that for **4c**; however, NMR observation indicates a more complex product mixture, due apparently to the higher lability of phosphine in **4a** and/or the triphenylphosphine congener of **10**, Compound **9** is observed along with a variety of products formed by direct reaction of dma with free PPh_3 (see footnote 12).

(11) ^1H NMR (benzene-d_6): (η^5-C_5H_5) s, δ 4.60 (5 H); $-[C_2(CO_2CH_3)_2]$ s, δ 3.53 (6 H); $-P(CH_3)_3$d($^2J_{^{31}P-^1H}$ = 10 Hz), δ 0.71 (9 H). **10** exhibits an intense visible absorption at 510 nm, the appearance of which was followed in the kinetic measurements.

(12) Dimethylacetylene dicarboxylate reacts rapidly with phosphines, even at −50 °C, thus precluding experiments in the presence of free phosphine. See, for example, N. E. Waite, J. C. Tebby, R. S. Ward, and D. H. Williams, *J. Chem. Soc. C*, 110 (1969).

(13) An alternate mechanism we cannot rule out would involve an 18-electron transition state with coordinated dma, PMe_3, and η^3-cyclopentadienyl.

(14) Alfred P. Sloan Fellow, 1976–1978.

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Structural Studies of Precursor and Partially Oxidized Conducting Complexes. 9. The New One-Dimensional Tetracyanoplatinates, $M_2[Pt(CN)_4](FHF)_{0.39}\cdot xH_2O$ (M = Rb, Cs), and a New Lower Limit for the Platinum-Platinum Separation (2.80 Å)[1]

Sir:

Although the prototype one-dimensional tetracyanoplatinate (TCP) conductors $K_2[Pt(CN)_4]X_{0.3}\cdot 3H_2O$, termed "KCP(X)" where X = Cl or Br, have been extensively studied,[2] all attempts to prepare a fluoride derivative have as yet been unsuccessful.[3] From neutron diffraction structure studies of KCP(Br)[4] and KCP(Cl)[5] we pointed out the importance of water molecule hydrogen bonding [H—O—H···$^-$N≡C and X^-] in stabilizing the KCP(X) structures. Presumably if interchain coupling is increased,[6,7] e.g., by inclusion of a strong hydrogen bond forming ion such as F^-, the one-dimensional properties might be so modified as to suppress the Peierls distortion in the Pt chain. In an attempt to increase interchain coupling in this manner we have prepared the new anion-deficient fluorine containing salts $K_2[Pt(CN)_4](FHF)_{0.30}\cdot xH_2O$ and $M_2[Pt(CN)_4](FHF)_{0.39}\cdot xH_2O$ where M = Rb or Cs, referred to here as MCP(FHF). Details regarding the preparation and characterization of CsCP(FHF) are presented here. The Cs and Rb complexes contain the shortest intrachain Pt-Pt separations (2.832 (1) and 2.798 (1) Å, respectively) yet observed in partially oxidized tetracyanoplatinate (POTCP) salts.

Derivatives of KCP(X) have generally been prepared by cocrystallization of the unoxidized Pt^{2+}, and the halogenated Pt^{4+} salt, in a 5:1 ratio to form the partially oxidized $Pt^{2.3+}$ salt. The synthesis of an analogous KCP(F) complex by this route has not been possible since the fluorinated Pt^{4+} salt apparently cannot be successfully prepared.[2] Utilizing an electrolytic process first reported by Terrey[8] for the preparation of $K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$, K(def)TCP, and extended recently by Miller,[9] we have now prepared lustrous metallic gold-colored crystals of $M_2[Pt(CN)_4](FHF)_y\cdot xH_2O$ (M = K, y = 0.30; M = Cs or Rb, y = 0.39). For the cesium analogue, a saturated solution of $Cs_2[Pt(CN)_4]$[10] is adjusted to pH ~2 using 18 M HF, CsF (99.9%) is added until the solution is saturated, and the solution is then electrolyzed (polyethylene beaker, Pt electrodes with ~5 mm separation) at ~1.5 V.[11] Lustrous metallic gold-colored crystals of $Cs_2[Pt(CN)_4](FHF)_{0.39}\cdot H_2O$ begin forming immediately at the cathode and grow to a length of ~5 mm within 24 h. These crystals are strikingly different in appearance from KCP(Br) or KCP(Cl) which have a metallic reddish bronze color. The crystals were washed with cold H_2O and two independent elemental analyses[12,13] yielded the results given in Table I.

Table I. Observed and Calculated Analyses for $Cs_2[Pt(CN)_4](FHF)_{0.39}\cdot H_2O$[a]

	Cs	Pt	C	N	H	F
Obsd[12]	43.69	33.96	8.19	7.28[b]	0.23	2.41
	43.67	34.04				2.39
Obsd[13]			8.18[c]	9.32[c]	0.17[c]	2.80[c]
			8.36[d]	9.39[d]		2.11[c]
						2.69[d]
						2.54[d]
Av	43.68	34.00	8.24	9.36[b]	0.20	2.49 ± 0.24
Calcd	44.46	32.63	8.04	9.37	0.40	2.49

[a] Emission spectrographic analyses[14] for metal content indicated only Cs and Pt were present with very faint traces (<0.001%) of Na and Rb. Elemental analyses for halogen other than F was 0.0%. [b] Nitrogen analyses from Galbraith Laboratories were consistently low and are not included in any subsequent calculations. [c] Prepared electrolytically at 0.6 V. [d] Prepared electrolytically at 1.5 V (battery).

The platinum oxidation state of +2.35 was determined by iodine-thiosulfate[14] titrations. However, the elemental analyses indicate the existence of twice the number of fluorine atoms per platinum as expected for a partially oxidized $Pt^{2.35+}$ complex containing F^- ions. Since the complex was prepared in a very acidic HF medium, we believe that fluorine exists as the bifluoride ion, $(FHF)^-$. The infrared spectrum[15] is complicated but it indicates that H_2O (not H_3O^+) may be present, although further structural study is required to confirm the presence of $(FHF)^-$. Preliminary single-crystal x-ray diffraction analysis on a Syntex $P2_1$ diffractometer revealed that CsCP(FHF) is body-centered tetragonal with $a = b = 13.057$ (2) Å, and $c = 5.665$ (1) Å. The Rb complex is also body-centered tetragonal, with $a = b = 12.689$ (2) Å and $c = 5.595$ (1) Å, while photographs of KCP(FHF) indicate a primitive tetragonal cell with $a = b = 9.80$ (2) Å and $c = 5.82$ (1) Å. In addition, x-ray powder photographs indicate that CsCP(FHF) is not isostructural with KCP(Br) which has a primitive tetragonal space group with $a = b = 9.907$ (3) Å, and $c = 5.780$ (2) Å. By contrast $Cs_{1.75}[Pt(CN)_4]\cdot xH_2O$ is monoclinic.[16]

Using Pauling's theory[17] of the metallic bond we have shown[18] that it is possible to *predict* metal-metal separations in TCP complexes if the degree of partial oxidation is known, and vice versa. The metal spacing in CsCP(FHF) may be calculated from the lattice constants ($c/2$) and we obtain Pt-Pt = 2.83 Å. From it we may calculate[18] the degree of partial oxidation n from $D(1) - D(n) = 0.600 \log n$, where $D(1)$ = 2.59 Å for Pt and $D(n)$ = 2.83 Å, and therefore $n_{\text{calcd}} = 0.39$. The calculated metal valence is therefore $Pt^{2.39+}$, which is in good agreement with that obtained from the elemental chemical analysis (0.39). The finding of a 2.83 Å Pt repeat separation, as opposed to 2.88 Å in KCP(Br) and 2.96 Å in K(def)TCP, is highly significant and shows that within the anion-deficient POTCP family it is possible to vary the metal-metal separation by appropriately changing the cation and anion which in turn affects the degree of partial oxidation. Most important, Pauling's equation qualitatively predicts a trend of higher partial oxidation resulting in a shorter Pt-Pt separation. This is the case for the series of POTCP complexes composed of CsCP(FHF) ($D(n)$ = 2.83 Å, n = 0.39), KCP(Br) ($D(n)$ = 2.88 Å, n = 0.30) and K(def)TCP ($D(n)$ 2.96 Å, n = 0.25). The RbCP(FHF) is anomalous to some extent, since its degree of partial oxidation based on analytical