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Catalysis by 18 + δ Compounds. Cyclooligomerization of Acetylenes Catalyzed by $Co(CO)_3L_2$

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The ability of 18 + δ complexes to act as homogeneous catalysts was tested by studying the cyclooligomerization reactions of alkynes using the $Co(CO)_3L_2$ complex as the catalyst (L_2 = 2,3-bis(diphenylphosphino)maleic anhydride). Cyclotrimerization occurred for $RC{\equiv}CR$, where R = Ph, CH_2OSiMe_3, and CO_2Me. No reaction was observed for R = H, CH_3, $SiMe_3$, or $CH_2CH_2CH_3$. It is proposed that the alkynes need to be activated with electron-withdrawing groups to prevent the formation of high-energy 19-electron reaction intermediates. Although the mechanistic data are not conclusive, it is proposed that the reactions follow an odd-electron pathway involving the interconversion of 17- and 19-electron species. The 18 + δ complexes are labile to ligand dissociation, and it is this feature that makes them potentially good catalysts. The importance of ligand lability was demonstrated by comparing the activity of the $Co(CO)_3L_2$ complex to that of its inert 18-electron counterpart, $Co(CO)_3L_2^+$; the 18-electron molecule was not catalytically active. The products of the reactions and the electrochemical potentials of the reactants are not consistent with an electron transfer-initiated pathway involving organic radicals.

Introduction

The interconversion of 17- and 19-electron species in organometallic radical chemistry is as prevalent as that of 16- and 18-electron species in even-electron systems.[1] Although the interconversions of 16- and 18-electron species are utilized extensively in homogeneous catalysis,[2] the analogous 17/19-electron conversions have yet to be exploited in catalysis. We and others have shown that 18 + δ complexes (a relatively stable variety of 19-electron complex[3]) are dissociatively labile,[3,4] a feature that makes these molecules attractive candidates for catalysts in odd-electron schemes. To test the catalytic capabilities of these molecules, we studied their ability to catalyze the cyclooligomerizations of acetylenes. Cyclooligomerizations were chosen for the initial study because many of the mechanistic features of this reaction (discussed below) can be mimicked by 18 + δ complexes.

Interest in the cycloaddition of alkynes has continued steadily since Reppe discovered the tetramerization of acetylene to cyclooctatetraene.[5,6] Since that initial discovery, cycloaddition reactions have been carried out catalytically using a number of metal complexes.[10] Among the most efficient and most intensively studied homogeneous catalysts are the $CpCoL_2$ complexes (L = phosphines, alkenes, or alkynes).[20,21] Scheme 1 shows a generally accepted cyclotrimerization mechanism using this complex. The reaction proceeds with the substitution of the two L ligands by two molecules of alkyne, followed by formation of a metallacyclopentadiene via oxidative coupling of the alkyne, coordination of another molecule of alkyne, and reductive elimination of the product. In all of the proposed mechanisms in the literature, regardless of the type of catalyst, the metallacyclopentadiene complex is always implicated as a key intermediate.[22] The reaction of the metallacyclopentadiene with an alkyne to yield the product may proceed by several different routes:[20] (1) insertion to form a metallacycloheptatriene; (2) Diels−Alder-type cycloaddition within the coordination sphere of the

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[4] (a) Schut, D. M.; Keana, K. J.; Tyler, D. R. *J. Am. Chem. Soc.* **1995**, *117*, 8939−8946. (b) Mao, F.; Tyler, D. R.; Keszler, D. *J. Am. Chem. Soc.* **1989**, *111*, 130−134.

[5] Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Justus Liebigs Ann. Chem.* **1948**, *561*, 1.

[6] The primary cycloaddition products for acetylene are cyclotrimers and cyclotetramers.[7−9]

[7] (a) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185. (b) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93.

[8] Hoogzand, C.; Hubel, W. *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; John Wiley and Sons: New York, 1977; Vol. 1.

[9] Jolly, P. W.; Wike, G. *The Organic Chemistry of Nickel*; Academic Press: New York, 1975; Vol. II, p 94.

[10] The metal complexes include those of tantalum,[11] niobium,[12] ruthenium,[13] rhodium,[14] cobalt,[15] iridium,[16] nickel,[17,18] copper,[19] and palladium.[20]

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[14] (a) Abdulla, K.; Booth, B. L.; Stacey, C. *J. Organomet. Chem.* **1985**, *293*, 103. (b) Borrini, A.; Diversi, P.; Ingrosso, G.; Lucherini, A.; Serra, G. *J. Mol. Catal.* **1985**, *30*, 181.

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[17] (a) Walther, D.; Braun, D. *Z. Chem.* **1988**, *28*, 106. (b) Alphonse, P.; Moyen, F.; Mazerolles, P. *J. Organomet. Chem.* **1988**, *345*, 209.

[18] Aalten, H. L.; Van Koten, G.; Riethorst, E.; Stam, C. H. *Inorg. Chem.* **1989**, *28*, 4140.

[19] Jhingan, A. K.; Maier, W. F. *J. Organomet. Chem.* **1987**, *52*, 1161.

[20] See ref 2, p 870.

[21] Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.

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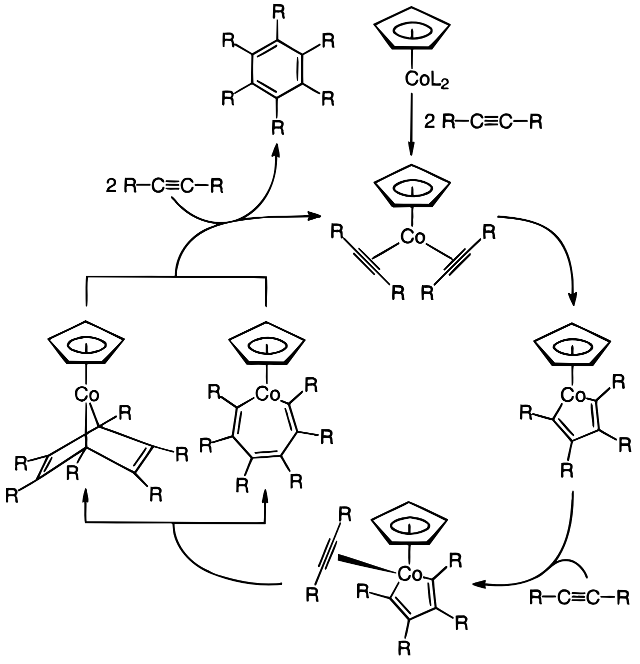
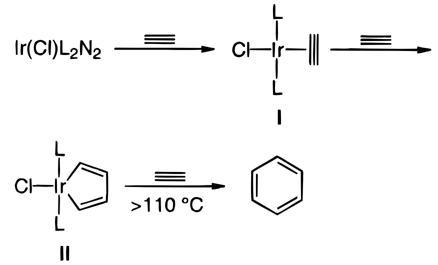
Scheme 1. Mechanisms for the Cyclotrimerization of Alkynes



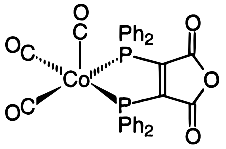
metal; (3) Diels−Alder-type cycloaddition without the prior coordination of the alkyne. However, it has proved difficult to distinguish between these mechanisms.

Two important features shared by most of the catalysts for alkyne cycloaddition are the ability to undergo facile ligand substitution and the ability to accommodate more than one alkyne ligand. For example, the catalytic reactivity of the $CpML_2$ complexes (M = Co, Rh) is at least partly attributable to the "coordinative flexibility" of the η^5-cyclopentadienyl ligand, which facilitates the substitution reaction.[14b,24] Likewise, Collman and Little's study on the catalytic reactivity of iridium complexes demonstrated the importance for the catalyst to coordinate multiple alkyne ligands.[16b,c] They showed that *trans*-$Ir(N_2)(PPh_3)_2Cl$ catalyzed the trimerization of activated acetylenes such as DMAD (dimethyl acetylenedicarboxylate) at 110 °C and that under moderate conditions the monoacetylene adduct (**I**) and the metallacyclopentadiene complex (**II**) could be isolated (Scheme 2). As expected, the carbonyl analogue, *trans*-$Ir(CO)(PPh_3)_2Cl$, is inactive as a trimerization catalyst, although a monoacetylene adduct is formed.[16b] Presumably the carbonyl ligand blocks the site necessary for coordination of a second acetylene ligand.

Scheme 2



The mechanistic features of the cyclooligomerization catalysts discussed above suggested to us that 18 + δ complexes are potential catalysts for this reaction. In particular, the lability of 18 + δ complexes may allow formation of a 19-electron complex with multiple alkyne ligands. Furthermore, the alkyne-substituted 19-electron complex may relieve its hyperelectronic saturation by undergoing an oxidative coupling of two alkyne ligands to form a 17-electron metallacyclopentadiene complex, which could then coordinate another alkyne ligand and lead to the product. In this note we report the catalytic cyclotrimerization of acetylenes using the $Co(CO)_3L_2$ complex[4,26] and its substituted derivative $Co(CO)_2(PPh_3)L_2$ as catalysts (L_2 = 2,3-bis(diphenylphosphino)maleic anhydride). Some mechanistic features of the reactions are also reported.



Results and Discussion

At room temperature, the $Co(CO)_3L_2$ complex reacts with a large excess of DMAD (alkyne:complex > 50:1) to form a dark brown solution in CH_2Cl_2. Preparative thin-layer chromatography of the product solution on silica gel followed by workup afforded a white solid, which was recrystallized from ethanol to give white needle crystals. This product was identified as hexamethyl mellitate, $C_6(CO_2Me)_6$, by its melting point, ^1H NMR, ^{13}C NMR, and mass spectroscopy (see Experimental Section).

Further experiments clearly showed that the formation of the hexamethyl mellitate was catalytic. Thus, when 116 mg of DMAD (8.16×10^{-1} mmol) was reacted with 9 mg of $Co(CO)_3L_2$ (1.48×10^{-2} mmol; alkyne:complex = 55:1) in 0.5 mL CH_2Cl_2 at room temperature for 2 days, 40 mg (9.4×10^{-2} mmol) of hexamethyl mellitate was obtained, corresponding to a 35% conversion from the alkyne to the benzene derivative. A 70% conversion was obtained when 116 mg DMAD (8.16×10^{-1} mmol) was mixed with 7 mg of $Co(CO)_3L_2$ (1.15×10^{-2} mmol; alkyne:complex = 71:1) in 0.5 mL CH_2Cl_2 at room temperature for 4 days, corresponding to about 0.17 turnover/h.

Mass spectroscopy showed the formation of some cyclooctatetraene product. Thus, in addition to the

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[22] Yamazaki et al. successfully isolated a series of cobalt cyclopentadiene complexes and showed that the isolated complexes are catalytically reactive.[23]

[23] Wakatsuki, Y.; Kiramitsu, T.; Yamazaki, H. *Tetrahedron Lett.* **1974**, 4549.

[24] It has been recognized for a number of years that ligand exchange in $CpM(CO)_2$ (M = Co, Rh) occurs by an associative mechanism in which η^5 to η^3 ring slippage takes place.[25] Likewise, studies on the catalytic reactivity of various derivatives of the $CpML_2$ complexes are consistent with ring slippage. For example, Abdulla et al. studied the electronic effect of substituted Cp rings in the $CpRhL_2$ (L = alkenes) complex on alkyne trimerization and found that the rate of alkyne trimerization increased in the following order: η^5-C_5Me_5 < η^5-C_5H_5 < η^5-C_5Cl_5.[14a] Borrini et al. investigated the catalytic properties of a number of indenyl and fluorenyl Rh(I) complexes and demonstrated that the indenyl and, in particular, the fluorenyl Rh(I) complexes show exceptionally high catalytic activity in alkyne trimerization when compared with the isostructural cyclopentadienyl Rh(I) complexes.[14b]

[25] (a) Schuster-Woldan, H. G.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 1657. (b) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908. (c) Cramer, R.; Seiwell, L. P. *J. Organomet. Chem.* **1975**, *92*, 245.

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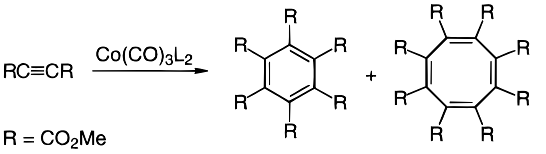
Table 1. Percent Conversion of Alkyne to Hexasubstituted Benzene as a Function of Substituent

substituent	temp (°C)	reacn time (h)	% conversion
$-$Ph	23	48	<1
$-$Ph	23	96	<1
$-$Ph	55	48	5
$-CO_2Me$	23	48	35
$-CO_2Me$	23	96	70
$-CO_2Me$	55	48	72
$-CH_2OSiMe_3$	23	48	92
$-CH_2OSiMe_3$	23	96	95
$-CH_2OSiMe_3$	55	48	95

benzene product (parent molecular ion at *m/e* 426 and a major fragment at *m/e* 395 (parent $-$ OMe)) there were three weak peaks at *m/e* 569 ($M^+ + 1$; $M^+ = C_8(CO_2Me)_8{}^+$), 537 ($M^+ -$ OMe), and 509 ($M^+ - CO_2Me$). However, the cyclooctatetraene derivative was formed in too small a yield to allow isolation (eq 1).



(1)

Reactions analogous to those with DMAD also occurred with PhC≡CPh and $Me_3SiOCH_2C{\equiv}CCH_2OSiMe_3$. (No cyclotetramer formed in these reactions, however.) The degree of conversion from the alkyne to the hexasubstituted benzene depended on the acetylene substituents. At room temperature, the percent conversion for a 55:1 solution of alkyne:$Co(CO)_3L_2$ catalyst was in the order Ph $\ll$ CO_2Me < CH_2OSiMe_3. The conversions for each of these compounds to the hexasubstituted benzene at room temperature over a 48 h period are as follows: <1%, 35%, and 92%, respectively. As expected, the conversions were higher with longer reaction times or higher reaction temperatures (Table 1). It is proposed that steric congestion in the incipient ring controls the rates of the reactions. For example, molecular modeling studies showed that, in hexamethyl mellitate, steric congestion forces the carbonyl groups out of the plane of the aromatic ring. Such bending will decrease the amount of π-overlap and increase the energies of the transition states along the reaction route.

Mechanistic Considerations. Reaction 1 only occurred with alkynes that are activated with electron-withdrawing groups (or at least not electron donating, in the case of CH_2OSiMe_3); no reaction occurred with R = H, CH_3, $SiMe_3$, or $CH_2CH_2CH_3$. This result follows logically from the stabilizing effect of electron-withdrawing ligands on $18 + \delta$ complexes.[4a] As demonstrated by us in several papers,[4] $Co(CO)_3L_2$ is substitutionally labile, and the first step of the reaction is proposed to be dissociative loss of CO to form the 17-electron intermediate $Co(CO)_2L_2$ (eq 2). Association of

$$Co(CO)_3L_2 \xrightleftharpoons{-CO} Co(CO)_2L_2 \xrightarrow{RC\equiv CR} Co(CO)_2L_2\,(RC\equiv CR) \quad (2)$$

an alkyne will then take place to form the substituted $18 + \delta$ compound. If the substituents on the alkyne are electron withdrawing, the substituted compound is stabilized relative to substituted compounds that do not have electron-withdrawing acetylenes. For the latter case, the acetylene-substituted compound is destabilized and further substitution is less likely to occur.

Figure 1. (A) ESR spectrum of the products of the reaction $Co(CO)_3L_2$ (1×10^{-3} M) + DMAD (4×10^{-3} M) in CH_2Cl_2 at room temperature. The multiline residual signal near the baseline is caused by a small amount of unreacted $Co(CO)_3L_2$ (see (b)). The ESR signal of the products is at least 100 times weaker than that of $Co(CO)_3L_2$ at the beginning of the reaction. (B) ESR spectrum of $Co(CO)_3L_2$ in THF at 25 °C.

In an attempt to elucidate other aspects of the catalytic mechanism, the reaction was carried out with a reduced alkyne/$Co(CO)_3L_2$ ratio. The ESR spectrum of the solution following the reaction of $Co(CO)_3L_2$ (1×10^{-3} M) with DMAD (4 x 10^{-3} M) showed that the ESR signal of $Co(CO)_3L_2$ had disappeared and was replaced by a much weaker signal (Figure 1a). The weaker ESR signal does not show a simple nuclear coupling pattern, probably due to the presence of more than one paramagnetic species that exist in small amounts and whose spectra overlap with each other. A concurrent ^1H NMR spectrum showed the appearance of phenyl proton peaks (at 7.2 ppm), suggesting the formation of a diamagnetic species containing the L_2 ligand.[27] Bubbling CO gas through the ESR tube containing the above solution resulted in the disappearance of the weak signal and the reappearance of the intense ESR signal of $Co(CO)_3L_2$ (Figure 1b). Likewise, a CO purge caused the ^1H NMR peaks at 7.2 ppm to disappear. Purging the ESR tube with N_2 made the weak signal reappear and the signal of $Co(CO)_3L_2$ disappear again. These results suggest that (1) the reaction of $Co(CO)_3L_2$ with DMAD converts the complex into a diamagnetic species along with some paramagnetic species that are present in small amounts and in equilibrium with the diamagnetic species and (2) the conversion between the $Co(CO)_3L_2$ complex and the diamagnetic species is reversible.

The reaction of $Co(CO)_3L_2$ (2×10^{-3} M) with DMAD (4×10^{-3}–8×10^{-3} M) was also monitored by infrared spectroscopy. Following mixing of the two solutions, the $Co(CO)_3L_2$ bands at 2080, 2031, 2009, 1742, and 1670 cm^{-1} (all strong) decreased in intensity and new bands grew in at 1987 (s, br), 1842 (w), 1812 (vw), 1775 (vs), 1744 (s), and 1699 (s) cm^{-1}. The band at 1987 cm^{-1} is assigned to a C≡O stretch, the bands at 1842, 1812, and 1775 cm^{-1} and their intensities relative to each other are characteristic of the C=O stretches of the L_2 ligand in an 18-electron complex (Table 2), and the two bands at 1744 and 1699 cm^{-1} are assigned to the carboxylic

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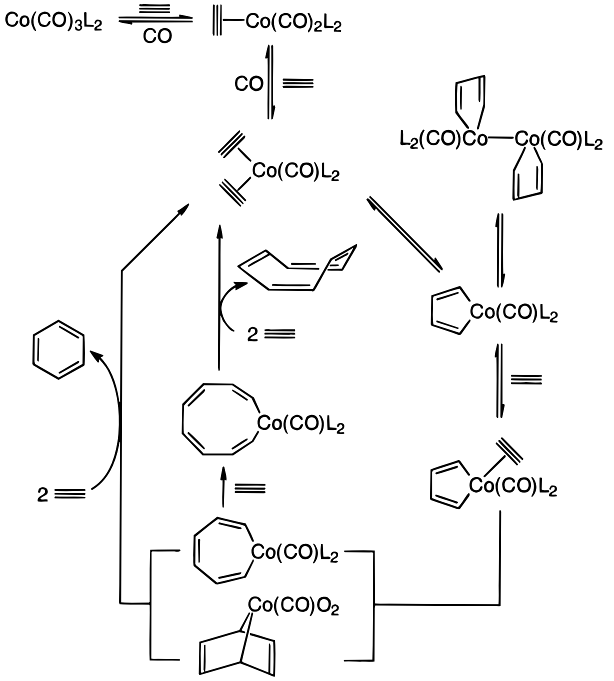
[27] The spectrum is possibly exchange-broadened because of a monomer−dimer equilibrium. However, a low−temperature (−80 °C) NMR experiment (at which temperature the exchange should be slower) did not reveal any new resonances.

Table 2. IR Data in CH_2Cl_2

complex[a]	ν(C≡O) (cm^{-1})	ν(C=O) (cm^{-1})
$Co(CO)_3L_2$	2080 (s), 2031 (s), 2009 (s)	1742 (s), 1670 (s)
$Co(^{13}CO)_3L_2$	2029 (s), 1980 (s), 1960 (s)	1748 (s), 1679 (s)
$Co(CO)_2L_2PPh_3$	2009 (m), 1954 (s)	1735 (s), 1657 (s)
L_2		1838 (m), 1816 (w), 1763 (s)
$[Co(CO)_3L_2]^+I^-$	2040 (w), 2017 (m), 1966 (s)	1845 (w), 1780 (s)
$[Co(CO)_2L_2PPh_3]^+[FeCl_4]^-$	2029 (m), 1979 (s)	1850 (w), 1783 (s)

[a] L_2 = 2,3-bis(diphenylphosphino)maleic anhydride.

Scheme 3. Tentative Mechanism for Cyclooligomerization Using $Co(CO)_3L_2$

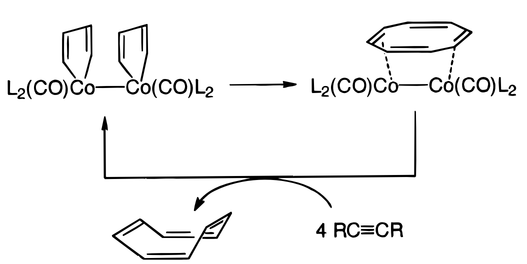


groups of coordinated DMAD. Thus, the infrared data are consistent with the ESR data, which indicates that the major species present in solution is diamagnetic. Bubbling CO gas through the solution containing these species replaced their IR bands with those of the $Co(CO)_3L_2$ complex, again indicating a reversible conversion between $Co(CO)_3L_2$ and the diamagnetic product.

On the basis of these experimental data, the mechanism in Scheme 3 is tentatively proposed. In this scheme, the substitutional lability of $Co(CO)_3L_2$ gives rise to mono- and diacetylene substituted species. The disubstituted complex undergoes an oxidative coupling of the alkyne ligands to form a 17-electron metallacycle complex, which dimerizes to form a diamagnetic complex. As suggested by the spectroscopic data, the cobalt dimer is the major product when a stoichiometric amount of $Co(CO)_3L_2$ is reacted with DMAD. (Co−Co bonds are weak,[28] and consequently the equilibrium in Scheme 1 involving the dimer and the radicals is reasonable.) Presumably, the disubstituted 18 + δ complex, the 17-electron metallacyclopentadiene complex, and the dimer are in equilibrium because the ESR and IR spectra showed that the conversion between $Co(CO)_3L_2$ and the diamagnetic complex is reversible. The substituted 18 + δ complexes and the 17-electron metallacycle complex may be responsible for the observed weak ESR signals.

Under catalytic conditions (i.e., in the presence of a large excess of DMAD), the 17-electron metallacycle complex reacts with another molecule of alkyne to yield a 19-electron adduct. The next steps are obscure, but literature precedents suggest that the final coupling will proceed by either an intramolecular "Diels−Alder" cycloaddition or by insertion of the alkyne followed by the reductive elimination of the product and the regeneration of the catalyst. As commonly accepted in the literature, the formation of the cyclooctatetraene derivative is achieved by insertion of another molecule of alkyne into the metallacycloheptatriene, followed by reductive elimination of the product.[29]

According to the mechanism in Scheme 2, the cobalt dimer retards the catalytic process by being in equilibrium with the reactive 17-electron catalytic intermediate. Wilke proposed that such bimetallacycle dimers may catalyze cyclotetramerization of alkynes via the coupling of the two neighboring metallacycles (eq 3).[30] However, we have no evidence to confirm or rule out such a possibility in this system.



(3)

Catalysis by $Co(CO)_2(PPh_3)L_2$. The $Co(CO)_2(PPh_3)L_2$ complex is also labile,[31] and it also catalyzes the trimerization of DMAD with an efficiency comparable to that of $Co(CO)_3L_2$. Presumably, the mechanism of the reaction follows Scheme 2. It is expected that both $Co(CO)_3L_2$ and $Co(CO)_2(PPh_3)L_2$ would show similar catalytic efficiency because both complexes are labile catalyst precursors[31] that do not participate in the cycle.

Attempted Catalysis by $Co(CO)_3L_2^+$. To illustrate the importance to the cyclotrimerization process of the labile ligands in the 18 + δ complexes, the catalytic properties of the $[Co(CO)_3L_2^+]$ 18-electron complex were studied. (Previous work showed that this compound is inert toward substitution.[4b]) Under the same reaction conditions as reaction 1, the $[Co(CO)_3L_2^+]I^-$ compound did not react with any of the alkynes used in this study within the time frame studied (96 h, eq 4).

$$R{-}C{\equiv}C{-}R \xrightarrow{[Co(CO)_3L_2{}^+]I^-} \text{No Reaction} \qquad (4)$$

An Electron Transfer Mechanism? Nineteen-electron complexes have two primary modes of reactivity: ligand dissociation and electron transfer.[1] An alternative pathway for reaction 1 thus might involve an electron transfer-initiated radical mechanism. However, two points strongly suggest an electron transfer mechanism is not involved. First, the product distribution is not that for a radical reaction because radical

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[28] Wilkinson, G.; Gillard, R. D.; McCleverty, J. A. *Comprehensive Coordination Chemistry*; Pergamon: Oxford, U.K., 1987; Vol. 1, p 289.

[29] See ref 2, p 613.

[30] Wilke, G. *Pure Appl. Chem.* **1978**, *50*, 677.

[31] The PPh_3 ligand is labile in the $Co(CO)_2(PPh_3)L_2$ complex. See ref 4b.

initiated oligomerizations of alkynes generally lead to straight chain polyacetylenes.[32] The products obtained in reaction 1 are strictly cyclooligomers with the primary product being the cyclotrimer. Second, the redox potentials of the 18 + δ complexes are not sufficient to initiate an electron transfer process. Alkynes generally have $E_{1/2}^{\text{redn}}$ values of −0.5 V vs SCE or less.[33] $Co(CO)_3L_2$ has an $E_{1/2}^{\text{ox}}$ of +0.07 V vs SCE.[4] Electron transfer from the $Co(CO)_3L_2$ complex to the alkynes is not probable.

Conclusions. The initiatory hypothesis for this study was that 18 + δ complexes would be useful catalysts because of their lability. This hypothesis was confirmed: it was demonstrated that the 18 + δ $Co(CO)_3L_2$ complex is a precatalyst for the cyclooligomerization of acetylenes. Mechanistic results suggest that an odd-electron pathway is involved in the reactions, but this point is not certain. These findings are important because they strongly suggest that the 17-/19-electron complex interconversion can be exploited for catalytic purposes.

Experimental Section

Materials and Reagents. All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere using standard Schlenk or vacuum line techniques or a Vacuum Atmospheres Co. glovebox. $Co(CO)_3L_2$ and $Co(CO)_2(PPh_3)L_2$ were synthesized as previously described.[4] Methylene chloride was distilled from CaH_2 under nitrogen. Dimethyl acetylenedicarboxylate (DMAD) was purchased from Alfa and purified by vacuum distillation (95−98 °C/19 mm). Silica gel (pore diameter 60 Å) plates for preparative thin-layer chromatography were obtained from Aldrich.

Equipment. Infrared spectra were recorded on either a Nicolet 5 DXB FT-IR or a Nicolet Magna 550 FT-IR, the latter interfaced and controlled by OMNIC software provided by Nicolet. Solution spectra were obtained using CaF_2 or NaCl plates while solid samples were obtained using KBr pellets. UV/vis spectra were collected with a Perkin-Elmer Lambda 6 UV/vis spectrophotometer interfaced with a computer running PECSS software.[34] ^1H and ^{13}C NMR data were collected with a GE-300 spectrometer operating at 300.15 MHz and 75.4808 MHz, respectively. EPR spectra were measured on a Bruker ESP 300 ESR spectrometer operating at X-band frequency with 100 kHz magnetic field modulation. Electron ionization mass spectra were obtained with a VG ZAB-2FHF mass spectrometer. The molecular modeling referred to in the text was done using HyperChem Release 2 for Windows (Autodeck, Inc.). The calculations were run on an IBM compatible 486 DX computer. Geometry optimization for each of the ligands was performed using the MM+ function with no options chosen. A Polar−Ribiere conjugate gradient was chosen to determine convergence for the local minima with the RMS gradient set at 0.1 kcal/(Å/mol) and conducted *in vacuo*.

1,4-Bis(trimethylsiloxy)-2-butyne. 2-Butyne-1,4-diol (1.012 g; 11.75 mmol) was weighed into a 100 mL round-bottom flask and suspended in 50 mL THF. The suspension was stirred, and triethylamine was added (3.3 mL; 23.7 mmol). Trimethylsilyl chloride was added dropwise (3.0 mL; 23.6 mmol), during which time a white precipitate appeared in solution. The reaction was exothermic and was allowed to proceed for 8 h. The solution was filtered to remove the precipitate ($[Et_3NH^+]Cl^-$), and the precipitate was rinsed with Et_2O. The Et_2O rinse was added to the THF solution, which was then dried over anhydrous $MgSO_4$. After filtering of the $MgSO_4$ from the solution, the solvent was removed under reduced pressure. The product was then purified by distillation under vacuum. During the distillation, the red color obtained during the reaction disappeared and the solution turned a faint yellow. All of the impurity was distilled over, leaving the product; yield, 1.89 g (70%). ^1H NMR (δ, acetone-d_6): 0.13 (s, 9H), 4.31 (s, 2H). ^{13}C NMR (δ, acetone-d_6): −0.95 (CH_3), 50.65 (CH_2), 84.03 (methyne carbons).

Cyclooligomerization Reactions. The cyclooligomerization reactions of DMAD were studied first. The reactions were carried out under nitrogen at room temperature in the glovebox. In a typical reaction, 100 μL of DMAD was mixed with 9.0 mg of $Co(CO)_3L_2$ in 0.5 mL of CH_2Cl_2. The solution was then left to sit in the glovebox for 2 days, during which time the color of the solution turned from green to dark-brown. Preparative TLC (silica gel, diethyl ether) of the above solution gave numerous colored bands and two colorless bands. The two colorless bands were separated from the rest of the bands and eluted with CH_2Cl_2 separately. After evaporation of the solvent, the solution of one colorless band gave the unreacted DMAD, and the solution of the other colorless band gave the white hexamethyl mellitate (35%), which was recrystallized from ethanol to yield white needle crystals: Mp 185.5−186.5 °C (lit. mp 185−186 °C); IR (KBr) 1739 (br, vs), 1445 (s), 1230 (s) cm^{-1}; ^1H NMR (CD_3Cl) δ 3.88 ppm (s); ^1H NMR (CD_2Cl_2) δ 3.86 ppm (s); ^{13}C NMR δ 165.1 (s, phenyl ring C), 133.9 (s, carbonyl C); 53.5 (q, methyl C); UV (THF) 241 nm (ϵ 5180). To check for the formation of the cyclooctatetraene derivative, a mass spectrum of the product mixture was obtained. The following major peaks are assigned to hexamethyl mellitate and the cyclooctatetraene derivative, respectively: hexamethyl mellitate, *m/e* 426 (M^+, 3%), 395 (M^+ − OMe, 100), 364 (8); the cyclooctatetraene derivative, *m/e* 569 (M^+ + 1, <1%), 537 (M^+ − OMe, 2), 509 ($M^+ - CO_2Me$, 3), 503 (<1%). The amount of the cyclooctatetraene derivative in the products was too small to allow isolation.

The cycloaddition reaction of DMAD catalyzed by $Co(CO)_2L_2$-PPh_3 was carried out in a similar fashion.

Subsequent cyclooligomerization reactions were carried out using a stock solution of $Co(CO)_3L_2$ (2×10^{-4} M; 24 mg in 200 mL C_6H_6 or CH_2Cl_2). Solutions of the alkyne were then added so as to make a 55:1 ratio of alkyne to $Co(CO)_3L_2$ solution. These solutions were then studied by IR, EPR, and ^1H NMR.

Spectroscopic data for the alkynes and the cyclotrimer products are reported below.

$Me_3SiOCH_2C{\equiv}CCH_2OSiMe_3$: ^1H NMR (C_6D_6) −0.08 (s, 9H), 3.77 (s, 2H); ^{13}C NMR (C_6D_6) 2.21 (CH_3), 51.05 (CH_2), 90.31 (methyne carbons).

$C_6(CH_2OSiMe_3)_6$: ^1H NMR (C_6D_6) −0.01 (s, 9H), 4.05 (s, 2H); ^{13}C NMR (C_6D_6) −0.07 (CH_3), 51.38 (CH_2), 132.09 (aromatic carbons).

DMAD: ^1H NMR (C_6D_6) 2.91 (s); ^{13}C NMR (C_6D_6) 53.04 (CH_3).

$C_6(CO_2CH_3)_6$: ^1H NMR (C_6D_6); 3.28 (s); ^{13}C NMR (C_6D_6) 52.73 (CH_3). As was the case with DMAD only the CH_3 carbons atoms were resolved in the ^{13}C NMR spectrum.

C_6Ph_6: NMR spectroscopy was not sensitive enough to find the small amount of this product that formed in the reaction with PhCCPh. The product was detected by mass spectroscopy (*m/z*): 534 (C_6Ph_6), 457 (C_6Ph_5), 380 (C_6Ph_4), 178 (Ph_2C_2), 101 (C_2Ph). The latter two peaks are attributed to starting material. The sum of the three product peaks was <5% of the sum of the two starting material peaks.

IR and ESR Studies following the Reaction of $Co(CO)_3L_2$ with DMAD. $Co(CO)_3L_2$ (105 mg, 0.17 mmol) was stirred with DMAD (43 μL, 0.35 mmol) in CH_2Cl_2 (10 mL) at room temperature. During the reaction, a stream of N_2 was

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(34) PECSS software was obtained from Perkin-Elmer.

passed through the reaction vessel to sweep away any CO formed in the reaction. Samples were taken at intervals to monitor the reaction by IR and ESR spectroscopy. To obtain the IR spectra, the reaction solution was used directly; for ESR spectra, the reaction solution was diluted by a factor of at least 100. After about 4 h of reaction, the IR bands of $Co(CO)_3L_2$ had disappeared, and the following bands appeared: 1987 (s, br), 1842 (w), 1812 (vw), 1775 (vs), 1744 (s), and 1699 (s) cm^{-1}. At the same time the ESR spectrum showed a weak new signal and an even weaker signal from some unreacted $Co(CO)_3L_2$ (Figure 1a). The intensity of the new ESR signal was at least 100 times weaker than that of $Co(CO)_3L_2$ at the beginning of the reaction. Attempts to isolate the reaction products failed.

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