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A Laser Flash Photolysis Study of Photochemical Carbonyl Substitution in $M(CO)_6$ (M = Cr, Mo, W) with 1,10-Phenanthroline

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Photoreactions of $M(CO)_6$ (M = Cr, Mo, W) with 1,10-phenanthroline (phen) have been investigated by laser flash photolysis. A transient spectrum due to $Cr(CO)_5$(phen), where phen ligates in a monodentate fashion, was observed. In the cases of Mo and W, the growth curve of the final product, $Mo(CO)_4$(phen), was found to accord with the kinetics of consecutive first-order reactions. These facts indicate that, even with a ligand as well-suited to bidentate bonding as phen, the coordination of $M(CO)_5$ to phen does not concert with the extrusion of the second carbonyl. Both these reactions, however, were found to be significantly accelerated compared with those for pyridine derivatives, suggesting a profound electronic interaction between the metal atom and the noncoordinated nitrogen in $M(CO)_5$(phen). The wavelength shift of the d–d band in $Cr(CO)_5$(phen) is also attributable to this interaction. However, at this stage, it cannot be concluded whether the interaction is coordination, that is, whether $M(CO)_5$(phen) can be considered as the 7-coordinate 20-electron complex of an associative substitution mechanism.

Introduction

The photochemical carbonyl substitution of group 6 metal carbonyls ($M(CO)_6$, M = Cr, Mo, W) is well established to start with decarbonylation by the absorption of light. The coordinatively unsaturated species so generated, $M(CO)_5$, reacts with a ligand, L, to give $M(CO)_5L$.[1]

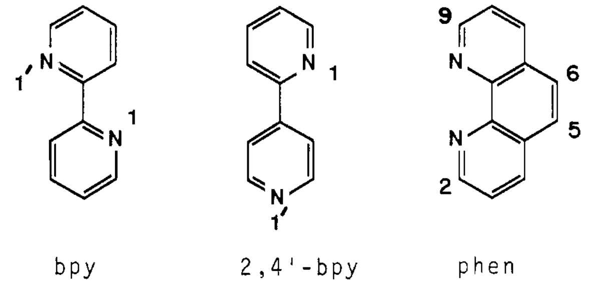
$$M(CO)_6 \xrightarrow{h\nu} M(CO)_5 + CO \qquad (1)$$

$$M(CO)_5 + L \rightarrow M(CO)_5L \qquad (2)$$

In the case of a bidentate ligand, does the elimination of the second carbonyl take place concertedly with the initial coordination?

$$M(CO)_5 + L \rightarrow M(CO)_4L + CO \qquad (3)$$

According to studies by Lees et al., the elimination of the second carbonyl does not occur concertedly with the coordination.[2-5] Indeed, in the case that a bidentate ligand can take a conformation where the direction of the second coordination point is not suitable for coordination, e.g., in the case of di-2-pyridylmethane, these authors were able to isolate $M(CO)_5L$, in which L ligates in a monodentate fashion. FT IR studies of the derivatives of 2,2′-bipyridine also suggest a stepwise mechanism including $M(CO)_5L$ where two nitrogens of 2,2′-bipyridines are not on the same side of the C_2–$C_{2'}$ bond in L.[6] The two nitrogens of 1,10-phenanthroline (phen) are constrained always to be geometrically suitable for bidentate ligation. We have examined, by means of laser flash photolysis, whether phen brings about the extrusion of the second carbonyl concertedly with the coordination.



Experimental Section

Materials. Samples of $M(CO)_6$ (M = Cr, Mo, W) were purchased from Aldrich Chemical Co. and were used without further

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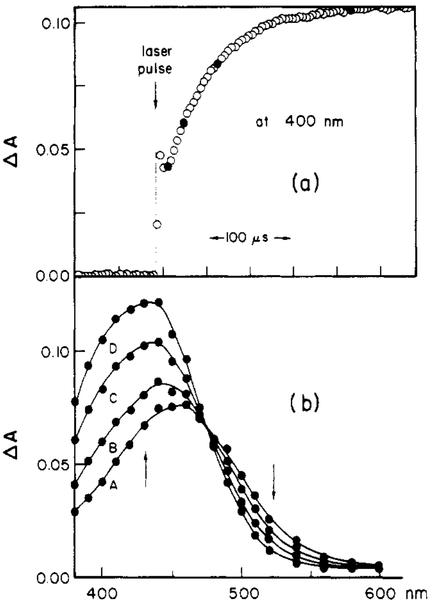

Figure 1. Laser flash photolysis of $Cr(CO)_6$ (1.8 mM) and phen (23.8 mM) in benzene. (a) A typical growth trace at 400 nm. Solid circles were for the spectra in (b). (b) Time-resolved differential spectra. A, B, C, and D correspond to 0, 19.5, 58.6, and 214.9 μs, respectively.

purification. phen, bpy, 2,4′-bpy, and 2,9-dimethyl-1,10-phenanthroline (Aldrich) were recrystallized from ethanol–water and dried on P_2O_5 in vacuo. Pyridine (Aldrich, Gold label) was distilled and dried with molecular sieves 4A. Benzene (Fisher Scientific, spectrophotometry grade) was purified with the usual sulfuric acid treatments, distillation, and an alumina column and stored on molecular sieves 4A.

Laser Flash Photolysis. A Molectron UV-400 nitrogen laser was used for excitation (337 nm, 3 mJ/pulse, 8 ns of pulse width). A right-angle optical system using a 10-mm cell was employed for the excitation-analyzing setup. All measurements were carried out at ambient temperature (24 ± 1 °C) and were the results of averages of at least four laser pulses. The estimated uncertainties in the rate constants obtained are ±20 %. Details of the kinetic spectrophotometer and data collection system are described elsewhere.[7,8] Samples were deaerated by bubbling argon (Linde, Ultra high purity grade) for 20 min and stirred with a magnetic stirrer during the experiment. A flow system was used for measuring transient spectra.

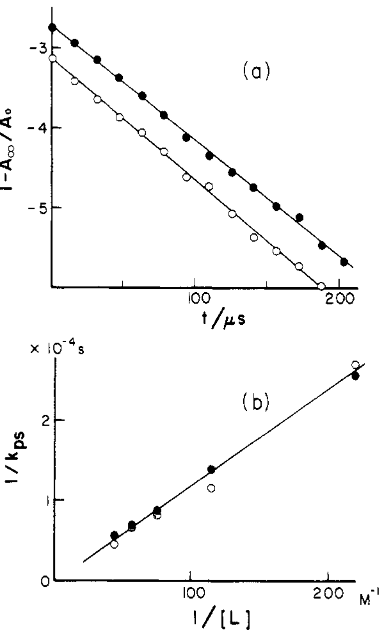

Figure 2. (a) Pseudo-first-order kinetics plots of decay (○) at 520 nm and growth (●) at 410 nm for $Cr(CO)_6$ (1.23 mM) and phen (17.8 mM) in benzene. (b) Plots of $1/k_{ps}$ vs 1/[L] based on eq 10.

Table I. Apparent Coordination Rate Constants of Pyridines and phen to $Cr(CO)_5$ in Benzene

	L			
	py	bpy	2,4′-bpy	phen
k_{app}, M^{-1} s^{-1}	1.2×10^5	2.1×10^4	1.5×10^5	8.2×10^5
λ_{max} ($Cr(CO)_5L$), nm	405	410	410	440
λ(measd), nm	400 (G)^a	400 (G)	400 (G)	410 (G)
	500 (D^a	500 (D)	500 (D)	520 (D)

^{a}Abbreviations: G, growth; D, decay.

Results and Discussion

Benzene solutions of $Cr(CO)_6$ (1.18 mM) and phen (23.8 mM) were deaerated by bubbling argon and then subjected to laser flash photolysis at 337 nm. The absorbance change at 400 nm is shown in Figure 1a. The fast decay immediately after the excitation pulse, which appears as a spike on the rising trace, is due to the decay of triplet phen generated by absorption of the excitation pulse.[9] Transient spectra (Figure 1b) are shown for times after this decay is completed. $Cr(CO)_5$ (λ_{max} = 620 nm) formed in perfluoromethylcyclohexane has been reported to convert swiftly to $Cr_2(CO)_{11}$ (λ_{max} = 480 nm).[10,11] A similar phenomenon has been observed in n-perfluorohexane, and, in the presence of benzene, $Cr(CO)_5$ reacts to give $Cr(CO)_5(B)$ (B = benzene) (λ_{max} = 460 nm), where benzene coordinates as a η^2-ligand.[12] Free $Cr(CO)_5$ was not observed in benzene solution with nanosecond time resolution; spectrum A in Figure 1b corresponds to $Cr(CO)_5(B)$.[13] In this concentration of phen, $Cr(CO)_5(B)$ changed into the second species within ~200 ns,[14] showing an isosbestic point at 470 nm. As shown in Figure 2a, both the growth at 410 nm and the decay at 520 nm obeyed pseudo-first-order reaction kinetics, and the reciprocals of the rate constants ($1/k_{ps}$) were approximately linear in 1/[phen], as described later. The second transient (λ_{max} = 440 nm) does not have the characteristic MLCT band[5] of $Cr(CO)_4$(phen) (519 nm), and no band is evident up to 800 nm. The photoreaction initiated by the laser pulse cannot be different from that initiated by continuous light, since the benzene solutions irradiated by a few tens of pulses of nitrogen laser showed the spectra of $Cr(CO)_4$(phen). The spectral change can be most plausibly explained by the idea that transient spectrum D is attributed to $Cr(CO)_5$(phen) in which phen ligates in a monodentate fashion. The phen ligand coordinates through its nitrogen. The possibility of Cr-$(CO)_5$(5,6-η^2-phenanthroline) can be eliminated by the fact

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[13] Spectra observed just after the laser pulse in benzene solutions of $M(CO)_6$ (λ_{max} = 460, 395, and 400 nm for M = Cr, Mo, and W, respectively) are not due to $M(CO)_5$ (solvent impurity). The impurity must be present more than ~0.125 M in concentration for completing the reaction of free $M(CO)_5$ within the duration of the laser pulse (8 ns $\gg$ 1/(k[impurity])), assuming even the diffusion-controlled rate for k (~10^9 M^{-1} s^{-1}). As written in the Experimental Section, benzene was purified specially to eliminate nucleophiles.

[14] The first transient (460 nm) produced by the photolysis of Cr(C-$O)_6$ alone in benzene did not show any change in its spectrum at this time scale. The second transient cannot be attributable to solvent impurities.

that appearance of the second transient was very slow when 2,9-dimethyl-1,10-phenanthroline replaces phen as the ligand.

In order to follow the second carbonyl extrusion from $Cr(CO)_5(phen)$, we monitored absorption at 520 nm following the spectrum D, since the MLCT band of $Cr(CO)_4(phen)$ appears at 519 nm.[5] However, only very slight growth was observed up to 3.5 ms. The rate constant of decarbonylation (k_{-CO}) in $Cr(CO)_5(phen)$ is roughly estimated to be less than 10^1 s^{-1}.

The absorption maximum of $Cr(CO)_5(phen)$ occurs at 440 nm, a longer wavelength than those of typical d–d bands of $Cr(CO)_5(py)$ (py = pyridine, 405 nm),[4] and $Cr(CO)_5(N^{1'}\text{-}\eta\text{-}2,4'\text{-bpy})$ (2,4′-bpy = 2,4′-bipyridine, 410 nm) (Table I). Distortions from octahedral coordination caused by a purely steric crowding around Cr cannot explain this shift because the absorption maximum of $Cr(CO)_5(bpy)$ (bpy = bipyridine) observed in the photolysis of $Cr(CO)_6$ with bpy occurs at 410 nm. The bpy ligand will promote comparable crowding around Cr, but the noncoordinated nitrogen does not face Cr.[6,15-19] We believe that the shift in $Cr(CO)_5(phen)$ is attributable to an electronic interaction between the noncoordinated nitrogen and Cr, which may give rise to distortion from a typical octahedral coordination.[20]

Considering that the dissociative process predominates in the thermal carbonyl substitution of $M(CO)_6$[21,22] and that $Cr(CO)_5(B)$ will dissociate B more easily than $M(CO)_6$ dissociates CO, reactions following the photochemical generation of free $Cr(CO)_5$ will be postulated as follows.[23,24]

$$M(CO)_5 + B \underset{k_{-B}}{\overset{k_b}{\rightleftarrows}} M(CO)_5(B) \qquad (4)$$

$$M(CO)_5 + L \xrightarrow{k_L} M(CO)_5(L) \qquad (5)$$

As the concentration of free $Cr(CO)_5$ is very low in benzene, the steady-state treatment can be applied to this system and gives eq 6.

$$\frac{d[M(CO)_5(B)]}{dt} = \frac{-k_{-B}k_L[L]}{k_B[B] + k_L[L]}[M(CO)_5(B)] \qquad (6)$$

If $k_B[B] \gg k_L[L]$ holds, eq 6 can be simplified to eq 7

$$\frac{d[M(CO)_5(B)]}{dt} = -k_{app}[L][M(CO)_5(B)] \qquad (7)$$

where

$$k_{app} = \frac{k_{-B}}{k_B[B]}k_L \qquad (8)$$

Therefore, the second-order rate constant (k_{app}), obtained from the plots of pseudo-first-order rate constants (k_{ps}) vs [L] on the basis of eq 7, consists of a term involving the equilibrium of solvent coordination ($k_{-B}/(k_B[B])$) and the real rate constant for complexation of L (k_L).[10,23,24] In this study, k_{app} was obtained from the plots of $1/k_{ps}$ vs $1/[L]$ based on

$$k_{ps} = \frac{k_{-B}k_L[L]}{k_B[B] + k_L[L]} \qquad (9)$$

$$\frac{1}{k_{ps}} = \frac{k_B[B]}{k_{-B}k_L}\frac{1}{[L]} + \frac{1}{k_{-B}} = \frac{1}{k_{app}}\frac{1}{[L]} + \frac{1}{k_{-B}} \qquad (10)$$

In the case of the reaction of $Cr(CO)_5$ with phen, the value k_{app} using eq 7 or 10 was found to be 8.4×10^5 or 8.2×10^5 M^{-1} s^{-1}, respectively, indicating that the approximation $k_B[B] \gg k_L[L]$ is appropriate. Values of k_{app} for py, bpy, and 2,4′-bpy are shown in Table I. Since the steric environment of N_1 in 2,4′-bpy is similar to that of N in bpy, k_{app} for N_1 in 2,4′-bpy can be estimated from the value of bpy. The significantly larger value of k_{app} for 2,4′-bpy can thus be attributed to complexation at $N_{1'}$. An electron-withdrawing 2-pyridyl substituent in 2,4′-bpy has no effect on k_{app}, as can be seen from the comparison with k_{app} for py. The value k_{app} for phen should be at most twice k_{app} for py because there are twice the possible coordination sites. Instead, k_{app}(phen) is 6.8 times larger than k_{app}(py). This indicates a rate enhancement due to the additional nitrogen. In the case of bpy, k_{app} is far smaller than that of py because of steric hindrance caused by the protons at $C_{3'}$ and C_3.[3] This contrasts with the fact that the lone-pair electrons of the adjacent nitrogen in phen assist the initial coordination.

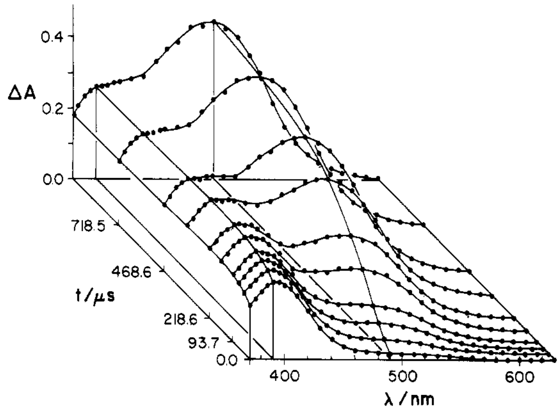

Figure 3. Time-resolved differential spectra for $Mo(CO)_6$ (1.24 mM) and phen (11.1 mM) in benzene.

Figure 3 shows the spectral change of benzene solutions of $Mo(CO)_6$ (1.24 mM) and phen (11.1 mM) after the excitation pulse. $Mo(CO)_5(B)$ (λ_{max} = 395 nm), present just after the pulse, converts to the final product, $Mo(CO)_4(phen)$, in ~1 ms.[13] A significant growth at 490 nm is due to the characteristic MLCT band of $Mo(CO)_4(phen)$.[3] If the reaction proceeds in accord with eq 3, since phen is present in excess, the growth should obey pseudo-first-order kinetics similar to the growth of $Cr(CO)_5(phen)$. Comparing Figure 4 with Figure 1, it is obvious that the growth of $Mo(CO)_4(phen)$ shows an induction period and is not well described as a pseudo-first-order reaction. Again, the extrusion of the second carbonyl does not occur concertedly with the initial coordination. The induction period in the appearance of the MLCT band reminds us

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(20) If we assume an octahedral wedge type or a pentagonal bipyramid type distortion,[39,40] the n orbital of the noncoordinated nitrogen will interact with one of the t_{2g} orbitals to raise its energy level. And the distortion from a regular octahedral lowers both or one of the e_g orbitals. Therefore, the d–d band of d^6 complex ($t_{2g} \rightarrow e_g$) is expected to shift to a longer wavelength.

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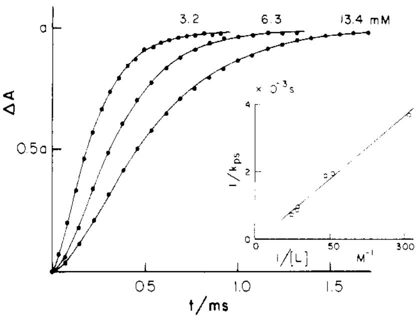

Figure 4. Growth traces (●) at 490 nm for $Mo(CO)_6$ (1.24 mM) and phen (3.2, 6.3, and 13.4 mM) in benzene and simulated curves for k_{ps} = 2700, 5400, and 14000 s^{-1}, respectively, and k_{-CO} = 5600 s^{-1}. Absorptions are normalized; a is 0.469, 0.477, and 0.472 for 3.2, 6.3, and 13.4 mM of phen, respectively. Inset: Plots of $1/k_{ps}$ vs $1/[L]$ based on eq 10.

Table II. Apparent Coordination Rate Constants and Rate Constants of the Second Carbonyl Dissociation

	k_{app}, M^{-1} s^{-1}			
$M(CO)_5$	L = phen	L = py	ratio[d]	k_{-CO}, s^{-1}
Cr	8.2×10^5	1.2×10^5	6.8	$<10^1$ >0.4[a]
Mo	7.9×10^5	5.4×10^4 [b,c]	14.6	5.6×10^3
W	3.6×10^4	3.3×10^3 [b]	10.9	4.6×10^2

[a] Reference 3. [b,c] Measured at 380 (growth) and 430 nm (decay), respectively. [d] See text.

of the generation of the final product in consecutive first-order reactions.[25]

$$\mathrm{Mo(CO)_5(B)} \xrightarrow{k_{ps}} \mathrm{Mo(CO)_5(phen)} \xrightarrow{k_{-CO}} \mathrm{Mo(CO)_4(phen)} \tag{11}$$

As shown in Figure 4, absorption changes at 490 nm were simulated by the method of Wiberg,[26] where only the final product, $Mo(CO)_4$(phen), was assumed to contribute to the absorption at 490 nm.

$$A_t = A_\infty[k_{-CO}(1 - \exp(-k_{ps}t)) - k_{ps}(1 - \exp(-k_{-CO}t))]/(k_{-CO} - k_{ps}) \tag{12}$$

A set of k_{ps} and k_{-CO} was determined which minimizes the average deviation from the observed absorbances. The plots of $1/k_{ps}$ vs 1/[phen] (Figure 4, inset) gave k_{app}. In the case of $W(CO)_6$ and phen, this procedure was done for the absorbance changes at 510 nm. Values of k_{app} and k_{-CO} for each metal are shown in Table II.

The direct comparison of k_{app} between the metals is meaningless because k_{app} contains a term for the solvent coordination equilibrium ($k_{-B}/(k_B[B])$), which varies from metal to metal. The rates k_{app} for phen are larger than those for py by 14.6 and 10.9 times in $Mo(CO)_5$ and $W(CO)_5$, respectively. The corresponding ratio for $Cr(CO)_5$ was calculated above as 6.8. The comparison of these values is valid because the term of solvent coordination has been canceled. The rate enhancement by the additional N is more effective in Mo and W than in Cr. Since the radii of coordination of Mo and W are almost the same and are larger than that of Cr (i.e., M–C lengths in $M(CO)_6$ are 1.915, 2.063, and 2.058 Å for Cr, Mo, and W, respectively[29,30]), the electronic interaction between the adjacent N and the metal must be stronger in Mo and W, and this explains the magnitude of the acceleration.

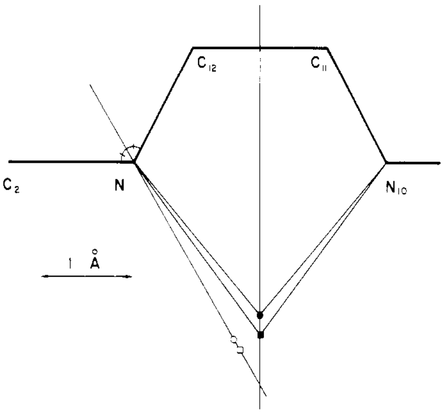

Figure 5. Molecular geometry around phen:[34-38] ●, $Cr(CO)_4$(phen) (Cr–N = 2.112 Å); ■, $W(CO)_4$(phen) (W–N = 2.228 Å); ○, $Cr(CO)_5$(phen); □, $W(CO)_5$(phen). In the latter two, M–N lengths of $M(CO)_5$(py) are used (Cr–N = 2.148 Å; W–N = 2.27 Å), and it is assumed that metal atom lies in the plane of phen and that $M–N_1$ bisects $C_2–N_1–C_{12}$ angle.

The rates of dissociation of the second carbonyl (k_{-CO}) in $M(CO)_5$(phen) are considerably greater, by at least 10^3 times, than those for $M(CO)_5$(bipyridines) reported in the literature.[3,6] Furthermore, the ordering of k_{-CO} (Mo > W > Cr) clearly differs from that of dissociative reactivity for $M(CO)_6$ and $M(CO)_5(L)$ (Mo > Cr > W).[22,31,32] These facts again suggest a strong electronic interaction between the noncoordinated nitrogen of phen and metal, especially in Mo and W.

The electronic interaction apparent in these reactions must exist in the transition species $M(CO)_5$(phen) itself, as observed in the longer wavelength shift of the d–d band in $Cr(CO)_5$(phen). As shown in Figure 5,[34-38] the geometry of $M(CO)_4$(phen) seems very close to that of $M(CO)_5$(phen) if we assume that the metal atom lies in the plane of phen and $M–N_1$ bisects the $C_2–N_1–C_{12}$ angle. However, in *cis*-$[Pt(Cl)(PPh_3)_2(phen)]^+$ (square 16-electron complex) where phen has been reported to ligate in a monodentate fashion, the angle corresponding to $M–N_1–C_2$ is so narrow that two considerably different Pt–N lengths can be observed (2.137 and 2.843 Å).[33] At this stage, it cannot be concluded whether or not the electronic interaction between the noncoordinated nitrogen and metal is simply coordination, that is, whether $M(CO)_5$(phen) should be considered as the 7-coordinate 20-electron complex of the associative substitution mechanism.[39,40]

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Registry No. Phen, 66-71-7; Py, 110-86-1; bpy, 366-18-7; 2,4′-bpy, 581-47-5; $Cr(CO)_5$, 26319-33-5; $Mo(CO)_5$, 32312-17-7; $W(CO)_5$, 30395-19-8; $Cr(CO)_5$(phen, 109906-81-2; $Mo(CO)_5$(phen), 113704-90-8; $W(CO)_5$(phen), 113704-91-9.

Intermolecular [2 + 2 + 2] Cycloaddition Reactions of Alkynes and Alkenes Mediated by Cobalt: X-ray Crystal Structures of Two Isomeric (η^5-Cyclopentadienyl)(η^4-1,3-cyclohexadiene)cobalt Complexes

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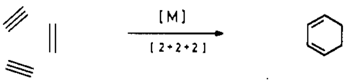
Treatment of bicyclic alkenes (norbornylene, *endo*-dicyclopentadiene) with alkynes (diphenylacetylene, dimethyl acetylenedicarboxylate) in the presence of $CpCo(CO)_2$ produced CpCo(η^4-1,3-cyclohexadiene) complexes (**1**, **2**, **6**, **7**, **10**, **11**) in good yields. Oxidation of complexes **1**, **2**, **6**, **7**, **10**, and **11** using $CuCl_2{\cdot}2H_2O$ afforded the free diene ligands **4**, **8**, and **13**. Further oxidation of **4** and **8** using ceric ammonium nitrate produced the aromatic derivatives **5** and **9**. The isomeric complexes **1** and **2**, which were obtained from *endo*-dicyclopentadiene and diphenylacetylene, were characterized by two-dimensional NMR spectroscopic techniques as well as X-ray crystallography. Complex **1** isomerized to **2** at 154 °C in a first-order process with an observed rate constant of $(1.5 \pm 0.1) \times 10^{-5}\ s^{-1}$. Treatment of norbornylene with diphenylacetylene in the presence of (η^5-$C_5H_4CH_3$)$Co(CO)_2$ produced two isomeric (η^5-$C_5H_4CH_3$)Co(η^4-1,3-cyclohexadiene) complexes (**14**, **15**). A 1:1 mixture of **1** and **14** isomerized intramolecularly to **2** and **15** in xylene-d_{10} at 155 °C. Both **1** and **2** are triclinic, $P\bar{1}$; **1** has unit cell parameters a = 10.943 (2) Å, b = 11.439 (1) Å, c = 14.954 (6) Å, α = 71.94 (3)°, β = 87.00 (3)°, γ = 62.27 (1)°, and D(calcd) = 1.30 g cm^{-3} for Z = 2. These values for **2** are a = 10.752 (1) Å, b = 12.640 (3) Å, c = 13.754 (3) Å, α = 69.89 (3)°, β = 66.83 (1)°, γ = 68.38 (1)°, and D(calcd) = 1.31 g cm^{-3} for Z = 2. Both were refined via least-squares, **1** to a conventional R value of 0.041 based on 4605 independent observed reflections ($[F_o \geq 5\sigma(F_o)]$ and **2** to 0.041 utilizing 3530 reflections. Each cobalt atom is η^5-coordinated to the cyclopentadienyl ligand (Co–Cp(av) = 2.09 (2) Å for **1** and 2.08 (3) Å for **2**) and η^4-bonded to the 1,3-cyclohexadiene ligand. The two exterior Co–C distances average 2.08 (3) Å in **1** and 2.07 (2) Å in **2**, whereas the two interior Co–C values average 1.97 (1) and 1.984 (8) Å, respectively.

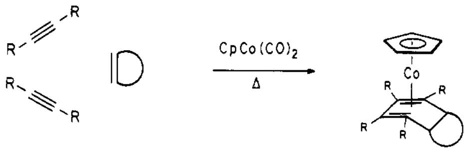
Introduction

The cyclooligomerization of alkynes and alkenes in the presence of transition-metal complexes has a rich and varied history.[1] Among these reactions studied is the [2 + 2 + 2] cycloaddition of two alkynes and one alkene to yield cyclohexadienes or metal-complexed cyclohexadiene adducts (eq 1). The reaction has been carried out catalytically by using iron,[2] rhodium,[3] nickel,[4] palladium,[5] or cobalt[6a] catalysts to produce free cyclohexadienes.



(1)

Moreover, the most extensively studied systems capable of promoting this cycloaddition reaction have been (η^5-cyclopentadienyl)cobalt (CpCo) complexes (eq 2).



(2)

Vollhardt and co-workers have pioneered the use of such complexes in intramolecular cycloadditions of enediynes,[6,7] intermolecular cyclizations of enynes and alkynes,[7a,c,8] and

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