contributions relative to the situation for C_6N_6.

In the absence of quantitative rate data for the individual k_4, k_5, and k_6 steps, our discussion by necessity must be speculative. For example, despite the rationale that k_5 should be faster for C_6N_6 than for its linkage isomer, it can also be argued that k_4 should be faster for C_5NCN_5, owing to the Co–NCR bond linkage being weaker than that of Co–CN. Certainly the fact that $Co(CN)_5CH_3CN^{2-}$ photoaquates only CH_3CN suggests this possibility, although photosubstitution quantum yield differences between $Co(CN)_6^{3-}$ and $Co(CN)_5CH_3CN^{2-}$ are small. However, attempts in this laboratory to observe emission from the LF states of the $Co(CN)_5X$ chromophore of both dimers and of the double salt $[Co(NH_3)_5H_2O][Co(CN)_6]$ were unsuccessful[19] under conditions (77 K) where emission is easily seen from $K_3Co(CN)_6$, suggesting that the presence of a proximate pentaamminecobalt(III) center does accelerate nonradiative deactivation.

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Registry No. $(NC)_5Co(\mu\text{-}CN)Co(NH_3)_5$, 22653-93-6; $(NC)_5Co(\mu\text{-}NC)Co(NH_3)_5$, 30233-29-5; $Co(CN)_5(NCCH_3)^{2-}$, 38684-02-5; $Co(CN)_5H_2O^{2-}$, 14842-83-2; $Co(NH_3)_5CN^{2+}$, 19529-81-8; $Co(NH_3)_5CH_3CN^{3+}$, 44819-13-8; $Co(CN)_6^{3-}$, 14897-04-2.

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Carbonyl Substitution Reactions of Cyclopentadienylbromodicarbonylruthenium(II) and (Ethyltetramethylcyclopentadienyl)bromodicarbonylruthenium(II). A Kinetic Study

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Reaction of $Ru(\eta^5\text{-}C_5Me_4Et)(CO)_2Br$ with phosphorus(III) ligands (L) in diethylene glycol dimethyl ether (diglyme) gives the monosubstituted derivative $Ru(\eta^5\text{-}C_5Me_4Et)(CO)LBr$ [L = $P(OPh)_3$, $P(OMe)_3$, or PPh_3]. Kinetic studies have shown that these reactions proceed via a dissociative mechanism. The corresponding carbonyl substitution reactions of $Ru(\eta^5\text{-}C_5H_5)(CO)_2Br$ with $P(OPh)_3$ or PPh_3 in diglyme also proceed via a dissociative mechanism although the previously reported reactions in di-*n*-butyl ether have been shown to involve free radicals. Comparison of the kinetic data for the two ruthenium compounds shows that the ethyltetramethylcyclopentadienyl compound is considerably more labile and that the $\eta^5\text{-}C_5Me_4Et$ ligand is able to stabilize the transition state and so promote ligand dissociation.

Substitution reactions of cyclopentadienylmetal compounds have been of special interest ever since Schuster-Woldan and Basolo studied the reactions of $[M(\eta^5\text{-}C_5H_5)(CO)_2]$ (M = Co, Rh, or Ir) and proposed that the cyclopentadienyl ligand promoted an associative pathway for carbonyl substitution reactions.(1) Since that time substitution reactions of one or more cyclopentadienyl transition-metal compounds from each group in the periodic table have been investigated,(2) including a report by one of us on the carbonyl substitution reactions of $[Mo(Cp')(CO)_3X]$ (I) [$Cp' = \eta^5\text{-}C_5H_5$; X = Cl, Br, or I].(3) In this latter study it was shown that modifying the cyclopentadienyl ring with a fused benzene substituent [i.e., I, $Cp' = \eta^5$-indenyl] had a dramatic effect on both the rate and mechanism of the carbonyl substitution reaction(4) while modifying the cyclopentadienyl ligand with a fused cyclohexane substituent [i.e., I, $Cp' = \eta^5$-tetrahydroindenyl] had only a minor effect.(5) Similarly, the ease of carbonyl substitution in the complexes $[Fe(Cp')(CO)_2I]$ increases in the order $Cp' = \eta^5$-tetrahydroindenyl $< \eta^5$-cyclopentadienyl $\ll \eta^5$-indenyl.(6)

Surprisingly, the only other systematic kinetic studies upon the effect of modifying the cyclopentadienyl ring appear to have been restricted to comparing (methylcyclopentadienyl)metal compounds with the corresponding unsubstituted-cyclopentadienyl compound; as might be anticipated, no significant effects upon the rate or mechanism of ligand substitution have resulted from such a minor modification.(7) We therefore decided to investigate the kinetics and mechanism of substitution reactions of bromodicarbonyl(ethyltetramethylcyclopentadienyl)ruthenium(II) (reaction 1) and

$$Ru(\eta^5\text{-}C_5Me_4Et)(CO)_2Br + PR_3 \rightarrow Ru(\eta^5\text{-}C_5Me_4Et)(CO)(PR_3)Br + CO \quad (1)$$

compare these results with those reported for analogous reactions of $[Ru(\eta^5\text{-}C_5H_5)(CO)_2Br]$.(8) Subsequent events led us to reinvestigate the reactions of the unsubstituted-cyclopentadienyl compound.

This study has additional significance in that (peralkylcyclopentadienyl)metal compounds are increasingly being used as homogeneous catalysts; for example, $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ catalyzes the hydrogenation of arenes,(9) $[Y(\eta^5\text{-}C_5Me_4Et)_2\text{-}n\text{-}Bu]$ catalyzes the polymerization of ethylene,(10) and $Ta(\eta^5\text{-}C_5Me_5)Cl_2(1\text{-octene})$ catalyzes the dimerization of α-olefins.(11)

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Table I. Rates of Reaction of Ru(C$_5$Me$_4$Et)(CO)$_2$Br with Phosphorus Donor Ligands in Diglyme

temp, °C	ligand	[ligand], M	10^5k_{obsd}, s^{-1}
88.6	PPh$_3$	0.160	1.74
		0.305	1.68
100.7	PPh$_3$	0.120	7.0
		0.267	7.2
		0.381	7.1
	P(OMe)$_3$	0.243	7.3
		0.580	7.2
	P(OPh)$_3$	0.105	6.8
		0.234	7.1
112.5	PPh$_3$	0.152	25.0
		0.229	27.5
		0.305	25.8

Table II. Rates of Reaction of Ru(C$_5$H$_5$)(CO)$_2$Br with Triphenyl Phosphite

temp, °C	solvent	[P(OPh)$_3$], M	10^5k_{obsd}, s^{-1}
115.3	diglyme	0.141	2.70
		0.310	2.70
125.4		0.122	8.7
		0.293	8.8
125.8		0.102	9.7
		0.208	9.4
135.3		0.099	29.2
		0.211	31.3
110.5	di-*n*-butyl ether^{a}	0.073	2.00
		0.153	1.92
		0.213	1.90
120.8		0.110	6.2
		0.209	6.4
		0.300	6.2
130.7		0.083	22.9
		0.149	22.1
		0.206	22.4

^{a} Containing duroquinone (0.012 M).

Table III. Thermodynamic Parameters for Carbonyl Substitution Reactions

complex	solvent	dielectric const	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}
Ru(η^5-C$_5$Me$_4$Et)(CO)$_2$Br	diglyme	7.23^{a}	132.0 ± 2.6	+27.0 ± 6
Ru(η^5-C$_5$H$_5$)(CO)$_2$Br	diglyme		155.9 ± 3.9	+67 ± 8
Ru(η^5-C$_5$H$_5$)(CO)$_2$Br	di-*n*-butyl ether^{b}	3.08^{c}	152.8 ± 4.2	+60 ± 10
Ru(η^5-C$_5$H$_5$)(CO)$_2$Br	di-*n*-butyl ether^{d}		122.6 ± 4.2	−8.9 ± 8.4

^{a} Value at 25 °C. I. P. Gol'dshtein, E. N. Gur'yanova, N. M. Alpatova, and Yu. M. Kesster, *Elektrokhimiya*, 3, 1011 (1967). ^{b} Containing duroquinone (0.012 M). ^{c} Value at 20 °C. R. Mecke, R. Joeckle, and G. Klingenberg, *Z. Elektrochem.*, 66, 239 (1962). ^{d} Data from ref 8.

Such (peralkylcyclopentadienyl)metal catalysts are usually more stable and hence have a longer lifetime, than the corresponding cyclopentadienylmetal catalysts; however, because of the paucity of data in this area, it is not known whether peralkylcyclopentadienyl ligands offer the additional advantage of increased reactivity relative to the unsubstituted-cyclopentadienyl ligand.

Experimental Section

Materials. The compounds [Ru(η^5-C$_5$H$_5$)(CO)$_2$Br][12] and [Ru(η^5-C$_5$Me$_4$Et)(CO)$_2$Br][13] were prepared by bromination of the corresponding cyclopentadienyldicarbonylruthenium dimer according to published procedures; both compounds were freshly recrystallized under nitrogen from a mixture of dichloromethane and hexane before use in kinetic studies.

Similarly, immediately prior to use in kinetic studies triphenylphosphine (BDH) was recrystallized under nitrogen from methanol, trimethyl phosphite (BDH) was distilled under nitrogen, and triphenyl phosphite (BDH) was distilled over sodium in a stream of nitrogen at reduced pressure. Duroquinone was recrystallized from ethanol.

Diethylene glycol dimethyl ether (diglyme) was refluxed with calcium hydride for several hours and then distilled under nitrogen shortly before use. Di-*n*-butyl ether was shaken with sodium sulfite solution to remove peroxides and dried first with calcium chloride followed by several hours reflux over calcium hydride and then distilled; immediately before use it was distilled under nitrogen from lithium aluminum hydride.

Kinetic Studies. Solutions of both the ligand and the compound [Ru(η^5-Cp')(CO)$_2$Br] [Cp' = C$_5$H$_5$ or C$_5$Me$_4$Et] were placed under nitrogen in aluminum foil wrapped flasks and thermostated in a constant-temperature bath (±0.1 °C). At zero time the solution of the ruthenium compound was added via a syringe to the ligand solution to give exactly 10 cm^3 of reaction mixture. Aliquots were subsequently withdrawn through a subaseal with the use of a syringe and transferred to a 1-mm KBr infrared cell. Reactions were followed by monitoring the disappearance of the highest frequency carbonyl stretching band of the complexes [Ru(η^5-Cp')(CO)$_2$Br] (Cp' = C$_5$H$_5$ or C$_5$Me$_4$Et) with use of a Perkin-Elmer 157G infrared spectrophotometer. Throughout the reaction a slow stream of nitrogen was passed over the reaction mixture.

Approximately 0.009 M solutions of ruthenium complexes were used, and in all cases the kinetic experiments were carried out under pseudo-first-order conditions with at least a tenfold excess of ligand. All reactions went to completion to give the corresponding monocarbonyl product (reaction 1); the products have all been isolated and fully characterized by elemental analysis, infrared spectroscopy, and ^{1}H and ^{13}C NMR spectroscopy[14] except for the known compound [Ru(η^5-C$_5$H$_5$)(CO)(P(OPh)$_3$)Br],[8] which was identified by spectroscopic techniques alone. Ionic products of the type [Ru(Cp')(CO)$_2$(PR$_3$)]Br or the disubstituted compounds [Ru(Cp')(PR$_3$)$_2$Br] were not formed in any of the reactions described herein.

Reactions were followed for at least 2.5 half-lives and found to give good linear plots of log [log (T_∞/T)] against time, *t*, where *T* and T_∞ are the transmittances of the reaction mixture at time *t* and at the end of the reaction, respectively. The slopes of these plots were computed by using a least-mean-squares error analysis, and the rate constants were found to be reproducible to 5%.

Results and Discussion

The rate of the carbonyl substitution reaction 1 for the ethyltetramethylcyclopentadienyl compound [Ru(C$_5$Me$_4$Et)(CO)$_2$Br] in diglyme was found to be independent of both the nature of the nucleophile and the nucleophile concentration (Table I). This together with the large positive entropy of activation indicates that this compound, in common with most other six-coordinate complexes of metal ions with the d^6 low-spin configuration, reacts via a first-order dissociative mechanism. To our surprise the activation parameters (Table III) were not too different from those reported for the corresponding unsubstituted-cyclopentadienyl complex [Ru(η^5-C$_5$H$_5$)(CO)$_2$Br] which was also found to undergo carbonyl substitution via a first-order dissociative mechanism.[8] Since, however, the latter activation parameters refer to reactions carried out in di-*n*-butyl ether and in xylene, we decided to investigate the reaction of [Ru(η^5-C$_5$H$_5$)(CO)$_2$Br] with phosphorus donor ligands in diglyme in order to have a direct comparison with the results obtained with [Ru(η^5-C$_5$Me$_4$Et)(CO)$_2$Br].

The reaction of triphenyl phosphite with [Ru(η^5-C$_5$H$_5$)(CO)$_2$Br] in diglyme produced [Ru(η^5-C$_5$H$_5$)(CO)(P(OPh)$_3$)Br] selectively and gave good linear first-order plots

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although the corresponding reaction with triphenylphosphine proved to be somewhat less reproducible. Therefore the reaction with triphenyl phosphite was studied in detail and our results (Table II) confirmed that this substitution reaction occurred via a dissociative process independent of the concentration of the incoming ligand. However, it was immediately apparent that this reaction was considerably slower than either those of the corresponding ethyltetramethylcyclopentadienyl complex in diglyme (Table I) or those reported[8] for the reactions of [Ru(η^5-C_5H_5)$(CO)_2$Br] in di-*n*-butyl ether. Further, the activation parameters reported for [Ru(η^5-C_5H_5)$(CO)_2$Br] in di-*n*-butyl ether were markedly different from those determined by us for the reaction of this compound in diglyme (Table III). Puzzled by this, and having checked that our results obtained in diglyme were reproducible, we decided to reinvestigate the reaction of [Ru(η^5-C_5H_5)$(CO)_2$Br] with triphenyl phosphite in di-*n*-butyl ether.

Unfortunately, despite careful purification of both the reactants and the solvent, we were unable to obtain consistent results. Rather, we observed an initial slow reaction followed by a rapid one which usually, although not always, "died away" after 60–80% reaction; the initial induction period before the fast stage of the reaction was totally irreproducible and varied from several minutes to several hours. Such behavior is characteristic of a radical reaction, and it has been noted previously that halogenometal carbonyl complexes such as [Mo(η^5-C_5H_5)$(CO)_3$X][3] and [Fe$(CO)_4X_2$][15] (X = Br or I) react with phosphites via a free radical mechanism. Therefore the reaction of triphenyl phosphite with [Ru(η^5-C_5H_5)$(CO)_2$Br] in di-*n*-butyl ether was repeated in the presence of a radical inhibitor (duroquinone), and this gave good linear reproducible rate plots (Table II). Further, the rates resembled the slow initial rates observed in di-*n*-butyl ether in the absence of a radical inhibitor and were comparable to those obtained in diglyme. Separate experiments confirmed that no reaction occurred when duroquinone and [Ru(η^5-C_5H_5)$(CO)_2$Br] were heated together in di-*n*-butyl ether. It was also shown that the product formed in the presence of duroquinone was the same as that formed in the absence of this radical inhibitor, namely, [Ru(η^5-C_5H_5)(CO)(P$(OPh)_3$)Br].

Summarizing, it appears that the previously reported[8] kinetics of the reaction of triphenyl phosphite with [Ru(η^5-C_5H_5)$(CO)_2$Br] in di-*n*-butyl ether refer to a radical reaction. In the more polar solvent diglyme or in the presence of a radical inhibitor in di-*n*-butyl ether, carbonyl substitution reactions proceed via a slow first-order dissociative process. Particularly striking is the fact that the cyclopentadienyl compound is much less reactive via a nonradical pathway than the corresponding ethyltetramethylcyclopentadienyl compound. For example, extrapolation of the activation plot reveals that at 100.7 °C [Ru(η^5-C_5Me_4Et)$(CO)_2$Br] undergoes carbonyl substitution reactions at a rate which is more than 18 times that of [Ru(η^5-C_5H_5)$(CO)_2$Br].

Inspection of the activation parameters (Table III) indicates that the greater reactivity of the ethyltetramethylcyclopentadienyl complex arises from a more favorable enthalpy term. There is no evidence to suggest that in the ground state the ruthenium–carbonyl bond in [Ru(η^5-C_5Me_4Et)$(CO)_2$Br] is weaker than that of [Ru(η^5-C_5H_5)$(CO)_2$Br]. Indeed one would anticipate the opposite since the electron-donating effect of the alkyl substituents should enhance the back-bonding to the carbonyl groups from the ruthenium atom, and this is supported by a comparison of the IR spectra of the two complexes [diglyme: Ru(C_5Me_4Et)$(CO)_2$Br, ν(CO) 2026 and 1967 cm^{-1}; Ru(C_5H_5)$(CO)_2$Br, ν(CO) 2052 and 1987 cm^{-1}]. Another indication that replacing a C_5H_5 ligand with a C_5Me_4Et ligand does not lead to weakening of a ruthenium–carbonyl bond comes from the X-ray crystal structures of [(μ-CO)$_2$(Ru(Cp′)(CO))$_2$] (Cp′ = η^5-C_5H_5[16] or η^5-C_5Me_4Et[17]); in both complexes the Ru–$CO_{terminal}$ bond lengths are the same within experimental error. Thus it appears that the more favorable enthalpy term for the compound [Ru(C_5Me_4Et)$(CO)_2$Br] is a result of a stabilization of the transition state.

One might argue that the enhanced reactivity arises from the steric effect of the ethyltetramethylcyclopentadienyl ligand. This implies that the Ru–CO bonds of the C_5Me_4Et complex are strained, and thus weakened, by steric congestion. However, there is no evidence to support this proposal, and, as previously stated, the IR spectra suggest that the Ru–CO bonds are actually stronger in [Ru(C_5Me_4Et)$(CO)_2$Br] than in [Ru(C_5H_5)$(CO)_2$Br]. Also, one would normally expect such a dominant steric effect to be clearly reflected in the entropy term whereas ΔS^* for the reaction of [Ru(η^5-C_5Me_4Et)$(CO)_2$Br] is actually more unfavorable than for [Ru(η^5-C_5H_5)$(CO)_2$Br] (Table III). This would seem to indicate that compared with the cyclopentadienyl compound the reaction of [Ru(C_5Me_4Et)$(CO)_2$Br] involves the formation of a more polar transition state with concomitant increase in solvation. The negative entropy term associated with such solvation thus reduces the positive entropy term expected for a dissociative process involving a bulky ethyltetramethylcyclopentadienyl compound.

It therefore appears that the favorable enthalpy term originates from an electronic effect of the ethyltetramethylcyclopentadienyl ligand. We suggest that the five alkyl substituents make the C_5Me_4Et ligand a potentially very powerful electron donor and that this cyclic aromatic ligand essentially acts as an electron reservoir. Thus as the carbonyl ligand with its lone pair of electrons dissociates from the ruthenium, the metal atom is compensated for the loss in bonding by increased interaction with the ethyltetramethylcyclopentadienyl ligand. Similar labilizing effects of electron-donor ligands have been observed previously; for example, the rate of carbonyl substitution in the complexes *cis*-[M$(CO)_4$Br(L)] (M = Mn or Re) increases with the donor ability of L [i.e., L = NC_5H_5 > PPh_3 > P$(OPh)_3$ ≈ CO].[18] Such effects are also thought to arise from the ability of a donor ligand L to stabilize the intermediate of reduced coordination number.[19]

It seems likely therefore that our observation that the ethyltetramethylcyclopentadienyl ligand promotes carbonyl dissociation can be extended to other (peralkylcyclopentadienyl)metal compounds which react via a dissociative mechanism. Thus, although (peralkylcyclopentadienyl)metal compounds have been used as catalysts because of their stability, an additional advantage may well be that they are actually more active than the corresponding unsubstituted-cyclopentadienyl compounds since ligand dissociation, for example, to created a free coordination site, is often a critical step in the catalytic cycle.

Registry No. Ru(C_5Me_4Et)$(CO)_2$Br, 72339-70-9; Ru(C_5H_5)$(CO)_2$Br, 32613-75-5; PPh_3, 603-35-0; P$(OMe)_3$, 121-45-9; P$(OPh)_3$, 101-02-0.

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