

tion was filtered to remove the catalyst through a pad of silica gel or filter paper using hexane-methylene chloride solvent as an eluent. Removal of the solvent under reduced pressure gave the corresponding hydrosilylating products. The yields are based on quantities obtained after this step. Some physical properties of the products are recorded below.

$\text{PhCH}_2\text{OSiEt}_3$: $^1\text{H-NMR}$ (CDCl_3) δ 7.28 (broad s, 5H), 4.72 (s, 2H), 0.97-0.68 (m, 15H). GC/Mass: no parent M^+ , 193 ($\text{M}^+ - \text{Et}$, 94), 163 (36), 135 (26), 91 ($\text{M}^+ - \text{OSiEt}_3$, 100), 65 (17). $\text{PhCH}_2\text{CH}_2\text{SiHPh}_2$: $^1\text{H NMR}$ (CDCl_3) δ 7.15 (broad s, 5H, benzylic ArH), 7.63-7.18 (m, 10H, Si ArH), 4.89 (t, $J=3.7$ Hz, 1H, SiH), 2.87-2.66 (m, 2H, Ph- CH_2), 1.63-1.37 (m, $-\text{CH}_2\text{Si}$). GC/Mass: no parent M^+ , 193 ($\text{M}^+ - \text{Et}$, 94), 163 (36), 135 (26), 91 ($\text{M}^+ - \text{OSiEt}_3$, 100), 65 (17). $\text{PhCH}_2\text{OSiMe}_2\text{Ph}$: $^1\text{H NMR}$ (CDCl_3) δ 7.68-7.20 (m, 10H), 4.69 (s, 2H), 0.39 (s, 6H). GC/Mass: no parent M^+ , 227 ($\text{M}^+ - \text{Me}$, 44), 197 (67), 164 (78), 149 (50), 135 (18), 91 (100), 65 (28). $\text{PhCH}_2\text{CH}_2\text{SiEt}_3$: $^1\text{H NMR}$ δ 7.1 (broad s, 5H), 2.48-2.70 (m, 2H), 0.3-1.3 (m, 17H). GC/MS, no parent M^+ , 191 (79) ($\text{M} - \text{Et}$) $^+$, 163 (42), 133 (7), 105 (10), 87 (100). $c\text{-C}_6\text{H}_{11}\text{OSiEt}_3$: $^1\text{H NMR}$ (CDCl_3) δ 2.01-1.54 (m, 11H), 1.19-0.58 (m, 15H). GC/Mass: 214 (M^+ , 27), 185 (100), 156 (33), 103 (60), 75 (66).

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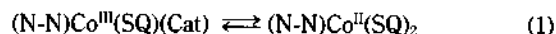
Distinct Oxidation-State Change Dependent on Remote Group of Coligand. $(\text{X}_2\text{-phen})\text{Co}(\text{3,6-DBBQ})_2$ ($\text{X}_2\text{-phen} = 4,7\text{-disubstituted-1,10-phenanthroline}$; $\text{3,6-DBBQ} = 3,6\text{-di-tert-butyl-1,2-benzoquinone}$)

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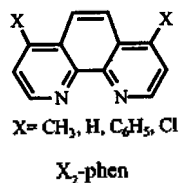
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Transition metal complexes containing quinone ligands have been elucidated to have metal- and quinone-localized electronic levels that are close in energy.¹ As a consequence, one of the most intriguing aspects of transition metal complexes of 1,2-semiquinonato (SQ) and catecholato (Cat) ligands is a unique facility for intramolecular electron transfer between the metal and chelated quinone ligands. This has been most prominently illustrated for the cobalt complexes, (N-N)Co^{III}(SQ)(Cat) where temperature- or photo-induced equilibria between the following redox isomers have been observed both in solution and in the solid state (1).² One isomer consists of Co(III) with one semiquinonato and one catecholato ligand and a diimine (N-N) ligand, and the other of Co(II) with two semiquinonato ligands and a diimine ligand. An intense band near 2500 nm (4000 cm^{-1}) assigned as Cat to Co(III) charge transfer has been characteristically observed for Co(III) forms.³⁻⁶ Moreover, for such complexes, the Co(III)/Co(II) transition temperature (T_c) has been found to be sensitive to the nature of the diimine coligands.⁶



In this paper, we describe an unexpectedly large change in oxidation state dependent upon the remote group X of

the following substituted phenanthroline coligands for a series of $(X_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$ (3,6-DBBQ=3,6-Di-*tert*-butyl-1,2-benzoquinone) along with temperature-dependence for a compound.



Experimental

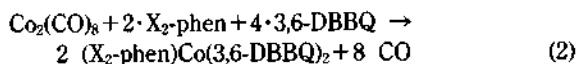
Materials and Instrumentation. Dicobaltoctacarbonyl ($\text{Co}_2(\text{CO})_8$) and $X_2\text{-phen}$ ($X = \text{Me}, \text{H}, \text{Ph}$) were purchased from Strem and Aldrich, respectively. 3,6-DBBQ was prepared according to literature procedures.⁷ $\text{Cl}_2\text{-phen}$ ligand⁸ and $(\text{H}_2\text{-phen})_2\text{Co}(3,6\text{-DBBQ})_2$ were prepared by the corresponding literature procedures. Elemental analysis (C,H,N) was carried out at the Korea Basic Science Center. Infrared spectra were obtained in 5000-400 cm^{-1} range on a Perkin Elmer 16F PC FTIR spectrometer with samples prepared as KBr pellets. Temperature-dependent electronic spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer equipped with a RMC-Cryosystems cryostat.

Synthesis of $(\text{Cl}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$. $\text{Co}_2(\text{CO})_8$ (171 mg, 0.50 mmol) and $\text{Cl}_2\text{-phen}$ (228 mg, 1.20 mmol) were combined in 30 mL of toluene. The mixture was stirred for 5 min, and 3,6-DBBQ (440 mg, 2.00 mmol) in 30 mL of toluene was added. The mixture was then stirred under a dinitrogen atmosphere for 2 h at room temperature. Evaporation of its solvent produced a dark blue solid in quantitative yield. The crude product was recrystallized in hexane to afford micro crystals. Found: C, 69.90; H, 6.45; N, 4.12. Calcd for $\text{C}_{40}\text{H}_{46}\text{N}_2\text{O}_4\text{Co}$: C, 70.17; H, 6.77; N, 4.09.

$(\text{Me}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$ and $(\text{Ph}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$ were prepared by the same procedure of $(\text{Cl}_2\text{-phen})_2\text{Co}(3,6\text{-DBBQ})_2$. Each crystal recrystallized gave satisfactory chemical analyses (C, H, N).

Result and Discussion

Synthetic procedures described in an earlier paper⁶ have been used to synthesize the present complexes: the reaction of $\text{Co}_2(\text{CO})_8$ with 3,6-di-*tert*-butyl-1,2-benzoquinone (3,6-DBBQ) in the presence of appropriate phenanthroline analogs ($X_2\text{-phen}$) smoothly afforded the products in toluene at room temperature (2).



IR spectra in the region of 5000-400 cm^{-1} at room temperature are designated in Figure 1. The title complexes show the characteristic bands at around 4000 cm^{-1} assigned as 3,6-DBCat to Co (3,6-DBCat=3,6-Di-*tert*-butyl-catecholato) charge transfer, which was found to exhibit in only Co(III) isomer.³ The band intensity is strongly dependent upon the remote functional group ($X = \text{Me}, \text{H}, \text{Ph}, \text{and Cl}$) of the phenanthroline coligands. For instance, the band of $(\text{Me}_2\text{-phen})$

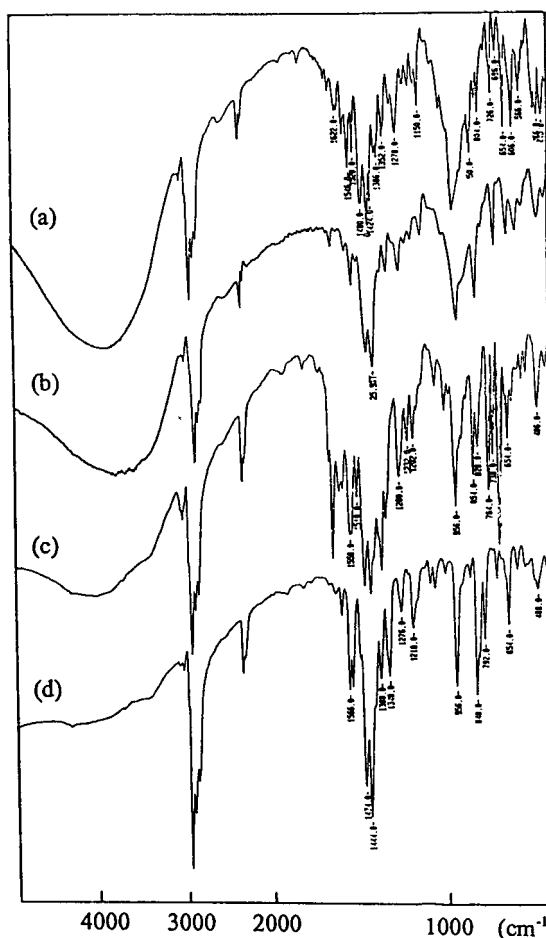


Figure 1. IR spectra of $(X_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$. (a) ($X = \text{CH}_3$), (b) ($X = \text{H}$), (c) ($X = \text{C}_6\text{H}_5$), (d) ($X = \text{Cl}$). The band around 4000 cm^{-1} is interesting and characteristic for the present complexes.

$\text{Co}(3,6\text{-DBBQ})_2$ is very strong whereas the corresponding band of $(\text{Cl}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$ is very weak in the region of around 4000 cm^{-1} . Furthermore, the respective intensity of $(\text{H}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$ and $(\text{Ph}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$ is median between both extreme bands. According to our previous paper, the band intensity indicates the ratio of the tautomeric forms $\text{Co(III)}/\text{Co(II)}$ at constant temperature.⁹ Thus, the IR spectra indicate that $(\text{Me}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$ predominantly exists as $(\text{Me}_2\text{-phen})\text{Co}^{\text{III}}(3,6\text{-DBS}^-\text{Cat})$ (3,6-DBS⁻=3,6-Di-*tert*-butyl-semiquinonato) at room temperature. In contrast, for $(\text{Cl}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$ system, the equilibrium is mostly shifted to $(\text{Cl}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-DBS}^-\text{Cat})$ at the same temperature. Such results are linearly correlated with Hammett constants of X group of the coligands (Hammett substituent constants (σ_{para}): $\text{Me} = -0.14$, $\text{H} = 0.00$, $\text{Ph} = 0.05$, and $\text{Cl} = 0.24$).¹⁰

$(X_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-DBS}^-\text{Cat})_2$ species is gradually increased with increase in Hammett constants. That is, Hammett constants that influence the equilibrium shown in eq. 1 provide fundamental insights on intramolecular metal-ligand electron transfer.

From above IR spectra, the cobalt complex containing $\text{Cl}_2\text{-phen}$ ligand was elucidated to exist predominantly as $(\text{Cl}_2\text{-phen})\text{Co}^{\text{II}}(3,6\text{-DBS}^-\text{Cat})_2$ in the solid state at room temperature.

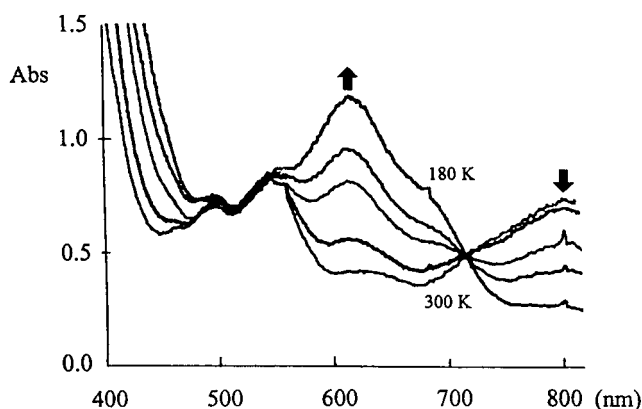


Figure 2. Temperature-dependent UV-vis spectra of $(\text{Cl}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$ in toluene solution.

In order to scrutinize the behavior of the cobalt(II) complex at low temperature, electronic spectra (400–820 nm) over the temperature range of 180–300 K were measured in toluene. The spectra of $(\text{Cl}_2\text{-phen})\text{Co}(3,6\text{-DBBQ})_2$ show reversible dependence upon temperature in solution (Figure 2). The band at 790 nm, characteristic of the low spin Co(III) species, decreases at reduced temperatures and is replaced by the transitions at 620 nm which is associated with the high spin Co(II) species.⁶ Thus, the electronic spectra recorded in toluene at temperatures where different tautomeric forms of the complex exist show features that are characteristic of the Co(III) and Co(II) charge distributions. Solution spectra at 210, 240, and 270 K show that at the respective temperature a mixture of Co(III) and Co(II) species exist at equilibrium. The temperature dependence of the solution spectra results from Co(III)/Co(II) transition via an intramolecular cobalt to catechol electron transfer.

In conclusion, the band intensity assigned cobalt to catechol charge transfer is linearly dependent upon Hammett constant of the 4,7-disubstituted 1,10-phenanthroline analogs. For such a bistability system, desirable charge distribution and tautomer equilibria may be anticipated from the Hammett constants. Equilibria between Co(III) and Co(II) tautomers in solution can be also controlled by temperature.

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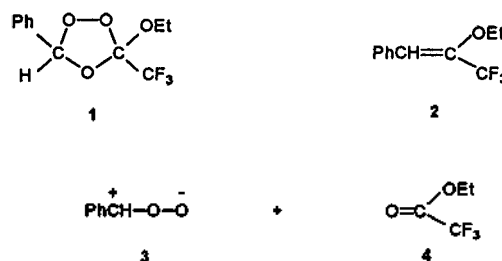
3-Trifluoromethyl-3-Phenyl-5,5-Dialkyl-1,2,4-Trioxolanes by Cross-Ozonolysis Reactions

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Ozonides of type 1 which bear trifluoromethyl substituents at the ozonide ring have been unknown until recently when the first representatives were prepared by ozonolyses of trifluoromethyl substituted olefins 2.¹ The formation of ozonides 1 could be explained *via* fragments 3 and 4.²



The fact, that vinylic chlorides,³ vinyl ethers,⁴ vinyl esters⁵ (5) and O-methylated oximes⁶ (6) are cleaved to give acyl chlorides, esters, anhydrides (12) and methyl nitrite (13), respectively, along with the complementary carbonyl oxides, could intimate cleavage of olefin 2 to give fragments 3 and 4 are formed. But the carbonyl oxides (7, 8) and carbonyl compounds (12, 13) do not undergo [3+2]-cycloadditions to give ozonides. The failure to afford the corresponding ozonides has been attributed to the low reactivity of the ensuing carbonyl compounds. In this paper we have tried to prepare trifluoromethyl substituted ozonides by reactions of more reactive trifluoroacetone (9) with carbonyl oxides (7, 8) which are generated from sources other than parent olefins 2, *viz.* by ozonolysis of enol esters 5 and O-methylated oximes 6.^{7,8} The method described here has the advantage that the enol ester 5 and the O-methyl oximes 6 are readily accessible from the corresponding carbonyl compounds.

Ozonolyses of the enol ester 5a-e in pentane at $-78\text{ }^\circ\text{C}$