

Photochemical and Thermal Reactions of Metal Carbonyls with Bis(ethoxythiocarbonyl) Sulfide: ESR of a New Class of Metal Carbonyl-Dithioketone Radical Complexes

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Although transition-metal carbonyl-1,2-diketo and *o*-quinone radical complexes have been extensively studied, the ESR characterization of transition-metal carbonyl-bis(ethoxythiocarbonyl) sulfide radical complexes represents the first report of metal carbonyl-dithioketone radical complexes. These complexes include the rare stable iron-organometallic complex $\text{Fe}(\text{CO})_5$ -BETS. Facile thermal substitution of organophosphorus ligands led to a further series of organometallic radical complexes.

Introduction

The existence of transition-metal carbonyl-1,2-diketone and *o*-quinone radical complexes has been known for some time. In particular, a variety of octahedral manganese-1,2-diketone radical complexes in which the manganese atom is coordinated to both ketoxygens have been studied extensively by ESR.¹⁻³ Analogous rhenium and tungsten radical complexes have also been characterized by ESR.⁴⁻⁶ Due to the high thermal stability of many of the rhenium-*o*-quinone radical complexes, we have made possible HPLC separation of these radical complexes for subsequent characterization by UV-visible, infrared, and fluorescence methods.^{4,7,8} Furthermore, these metal carbonyl-diketone and *o*-quinone radical complexes have been shown to undergo thermal exchange between the carbonyl group and group SA organometals. The daughter-substituted radical complexes resulting from the exchange have been extensively studied by ESR and optical methods.^{2,3,7-9} A class of optically active metal-quinone radical complexes has recently been generated by using chiral quinones and/or optically active ligands in the substitution reactions,⁷ which exhibit a fair degree of stereoselectivity.¹⁰

To date there have been no reports of the observation and identification of the corresponding metal carbonyl-dithioketone radical complexes in which the transition metal is coordinated to *two sulfur* atoms. The analogous thio-*o*-quinones are not readily available, and they may be too chemically reactive to interact with the metal carbonyls to form stable radical complexes. In this paper we report the first ESR characterization of a new class of transition-metal carbonyl-1,3-dithioketone radical complexes generated by photochemical and/or thermal reactions of the parent metal carbonyl with bis(ethoxythiocarbonyl) sulfide. While this class of metal radical complexes is fairly persistent at room temperature for up to a few hours, it is noteworthy that for the first time we have been able to produce and identify an iron carbonyl-1,3-dithioketone radical complex with excellent resolution of the ¹³C hy-

perfine coupling constant in liquid solution at room temperature. Facile thermal substitution of CO in these series of radical complexes also led to the formation and ESR characterization of some organophosphorus-substituted daughter radical complexes.

Experimental

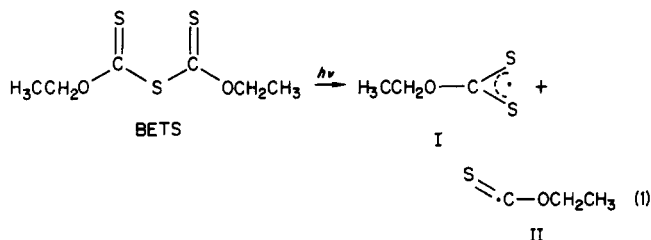
ESR spectra were recorded on a Varian E104 X-band spectrometer with 100-kHz field modulation. *g* factors were measured by using a Hewlett-Packard electronic frequency counter to monitor the microwave frequency and a standard DPPH sample to calibrate the field. In a typical experiment a sample consisting of several milligrams each of bis(ethoxythiocarbonyl) sulfide and the specific metal carbonyl in a 1-mL solution of toluene was degassed with nitrogen and sealed off in a Pyrex tube. The sample was irradiated in situ within a temperature probe in the microwave cavity by a 200-W super pressure mercury arc for a period of 10-15 s. The ESR signal and the lifetime of the radicals were processed by a Nicolet 4094 computer oscilloscope and directly plotted out on a Hewlett-packard graphic plotter.

Bis(ethoxythiocarbonyl) sulfide was purchased from Alfa Chemicals and was used in the experiments as received. Other chemicals were supplied by Strem Chemicals and Aldrich. Toluene was refluxed over sodium and distilled before use.

Results and Discussion

The Photolysis of Bis(ethoxythiocarbonyl) Sulfide.

The photolysis of a toluene solution containing bis(ethoxythiocarbonyl) sulfide, BETS, gave a continuous-wave ESR spectrum consisting of a well-resolved triplet due to two equivalent protons ($a_H = 2.71$ G; $g = 2.0038 \pm 0.0001$). This signal decayed rapidly upon termination of irradiation. The decay followed a first-order kinetic law, and the half-life of the radical species was measured by the Nicolet 4094 computer oscilloscope to be 160 ms. Since carbon-sulfur single bonds are susceptible to photochemical cleavage, the ESR results are consistent with reaction 1.



While both radicals I and II are expected to give a triplet spectrum due to the two methylene protons, the lifetime of the ESR signal strongly indicated that the observed species is radical I. The counter-radical II being a σ radical would not be expected to live long enough at room temperature for ESR observation.

(1) Foster, T.; Chen, K. S.; Wan, J. K. S. *J. Organomet. Chem.* 1980, 184, 113.

(2) Alberti, A.; Camaggi, C. M. *J. Organomet. Chem.* 1978, 161, C63.

(3) Alberti, A.; Camaggi, C. M. *J. Organomet. Chem.* 1978, 181, 355.

(4) Creber, K. A. M.; Wan, J. K. S. *J. Am. Chem. Soc.* 1981, 103, 2101.

(5) Weir, D.; Wan, J. K. S. *J. Organomet. Chem.* 1981, 220, 323.

(6) Creber, K. A. M.; Ho, T.; Depew, M. C.; Weir, D.; Wan, J. K. S. *Can. J. Chem.* 1982, 60, 1504.

(7) Ho, T.; Creber, K. A. M.; Wan, J. K. S. *J. Am. Chem. Soc.* 1981, 103, 6524.

(8) Creber, K. A. M.; Wan, J. K. S. *Can. J. Chem.* 1983, 61, 1017.

(9) Creber, K. A. M.; Wan, J. K. S. *Chem. Phys. Lett.* 1981, 81, 453.

(10) Creber, K. A. M.; Wan, J. K. S. *Transition Met. Chem. (Weinheim, Ger.)* 1983, 8, 253.

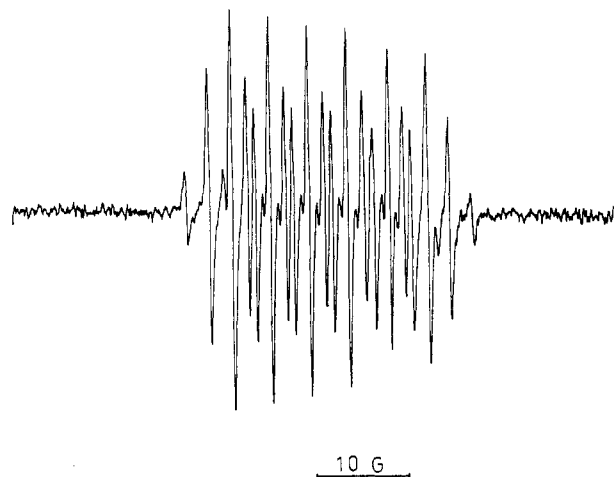
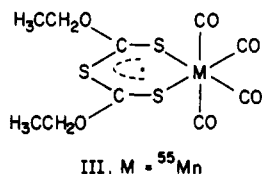


Figure 1. The ESR spectrum of a $\text{Mn}(\text{CO})_4$ -BETS radical complex in toluene at 23 °C.

Table I. ESR Parameters of Transition-Metal Carbonyl-BETS Radical Complexes in Toluene at 23 °C

radical complex	g factor	a_{metal} , G	$a_{\text{H}}(4 \text{ H})$, G
III, M = Mn	2.0095 ± 0.0001	4.13	2.46
III, M = Re	2.0060	17.70	2.46
VI, M = Mo	2.0060	7.87	1.5
VII, M = Fe	2.0078	11.20 (^{13}C)	2.40

The Photolysis of Metal Carbonyls in the Presence of BETS. Prolonged irradiation of a toluene solution containing both $\text{Mn}_2(\text{CO})_{10}$ and BETS would lead to the observation of only radical I, as the metal-BETS radical complexes are destroyed by light. Short pulses of irradiation between 10 and 15 s were sufficient to produce a good ESR spectrum due to a new species. The spectrum, which is relatively stable in the dark, exhibits six groups of quintets arising from one ^{55}Mn nucleus ($I = 5/2$) and four equivalent protons (methylene groups from BETS). A typical spectrum is shown in Figure 1, and the hyperfine coupling constants are given in Table I. The assignments are consistent with structure III. The two methylene



groups in the BETS ligand are equivalent and thus give a quintet splitting. Structure III is similar to the Mn-1,2-diketone radical complexes proposed by Aberti and Camaggi,^{2,3} and the *o*-quinone radical complexes reported by Foster, Chen, and Wan.¹ Many diamagnetic complexes such as the transition-metal 1,3-dithiocarbamates also exhibit a similar structure.¹¹

Compared to some Mn-centered radical reported by Kidd, Chen, and Brown¹² that have g factors as high as 2.03, the lower value of 2.0095 associated with structure III indicates considerable spin delocalization onto the BETS ligand. Significant spin delocalization onto the ligand, which is characteristic of coordination through S rather than through oxygen, is further supported by the

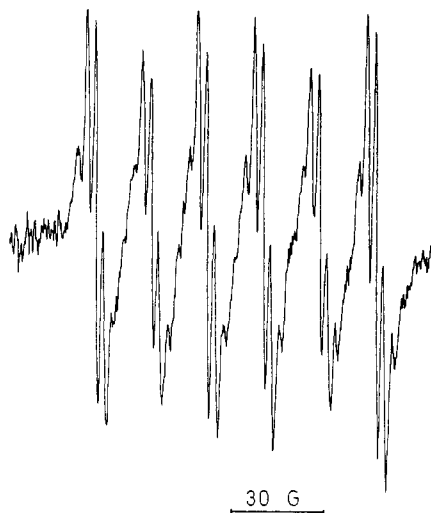
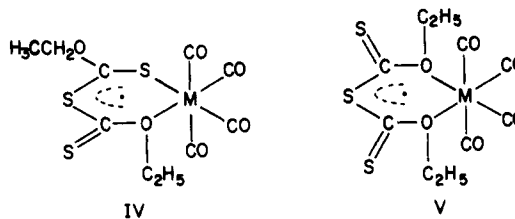


Figure 2. The ESR spectrum of a $\text{Re}(\text{CO})_4$ -BETS radical complex in toluene at 23 °C.

magnitude of the ^{55}Mn coupling constant that is even smaller than those observed for Mn-1,2-diketone radical complexes.^{1,3}

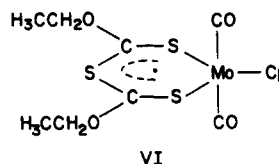
While structure III is consistent with the ESR assignment, other possible structures of such a radical complex include IV and V. In structure IV, the two methylene



groups of the BETS ligand would not be equivalent unless there is a rapid dynamic interchange process averaging the two configurations. Experimentally, we have examined the ESR spectrum over a temperature range between -20 and 80 °C. There was no evidence of such a process. Structure V represents a radical complex of Mn with a 1,3-diketone ligand. The extensive study by Alberti and Camaggi³ has found no evidence that such a stable 1,3-diketone radical complex could be observed.

When $\text{Re}_2(\text{CO})_{10}$ was used in the photolysis the corresponding radical complex with a structure III was observed by ESR. The rhenium radical complex is much more stable than the Mn analogue, and it has a lifetime of over 3 h at room temperature; the greater thermal stability of the rhenium complex is consistent with coordination through sulfur. A typical spectrum is shown in Figure 2. The characteristic line width effect among the rhenium hyperfine lines is similar to that observed in the rhenium-*o*-quinone radical complexes.⁹

In the photolysis of $(\text{Mo}(\text{CO})_3\text{Cp})_2$ with BETS in toluene, an evolution of a gas was observed together with an ESR spectrum consisting of six quintets ($^{95,97}\text{Mo}$, $I = 5/2$). The ESR assignments of the hyperfine coupling constants of a radical complex consistent with structure VI are given in Table I. Although gas evolution was also observed with



the other metal carbonyls, in this case it suggests dis-

(11) Bond, A. M.; Martin, R. L. *Coord. Chem. Rev.* 1984, 54, 23 and references therein.

(12) Kidd, D. R.; Cheng, C. P.; Brown, T. L. *J. Am. Chem. Soc.* 1978, 100, 4103.

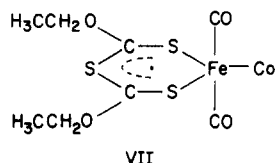
Table II. ESR Parameters of Organophosphorus Ligand Substituted Mn and Re Carbonyl-BETS Radical Complexes in Toluene at 23 °C

radical complex	P ligand	<i>g</i> factor	<i>a</i> _{metal} , G	<i>a</i> _P , G	<i>a</i> _H (4 H), G
Mn(CO) ₄ ·-BETS	PPh ₃	2.0096 ± 0.0001	5.55	43.7	2.17
	(Ph ₂ P) ₂ CH ₂	2.0095	5.60	46.5	2.12
	(-)-DIOP	2.0096	5.87	44.8	2.13
	(MeO) ₃ P	2.0100	9.24	54.2 ^a	1.90
	(PhO) ₃ P	2.0096	5.51	49.2	2.20
Re(CO) ₄ ·-BETS	PPh ₃	2.0052	21.7	32.7	2.46
	(Ph ₂ P) ₂ CH ₂	2.0063	21.6	33.1	2.50
	(-)-DIOP	2.0070	22.1	33.9	2.48

^a Two equivalent P.

placement of CO rather than the Cp ligand from (Mo(CO)₃Cp)₂ when the radical complex was formed. The radical complex VI was much less thermally stable than the Mn and Re analogues. Its half-life was about 120 s at room temperature.

In addition to the photochemical reactions reported above, we have examined the thermal reaction of Fe(CO)₅ with BETS in toluene at room temperature. The reaction was fast, leading to a large ESR signal of a quintet due to the four methylene protons of the BETS ligand. The thermal reaction was accompanied by gas evolution and a color change from yellow to brown. Under higher ESR sensitivity, the central quintet was resolved to be accompanied by two small outer groups of quintets, due to the 2% magnetic isotope of ¹³C (*I* = 1/2). The ¹³C hyperfine splitting and other ESR parameters of this iron-BETS radical complex are given in Table I. The ESR assignments are consistent with structure VII. The low *g* factor



of the iron-BETS radical complex, *g* = 2.0078, indicates substantial spin delocalization among the six-member ring. Other iron-centered radicals have been reported by Lionel, Morton, and Preston¹³ to have *g* factors as high as 2.05.

It is noteworthy that Fe(CO)₅ interacts thermally with BETS to form a stable radical complex. It is further interesting to note that a well-resolved ¹³C hyperfine splitting is readily observed in this complex. Few iron-organo radical complexes have been observed by ESR at room temperature, and rarely the Fe hyperfine could be resolved. The facile thermal displacement of CO from Fe(CO)₅ by BETS should be of some biological interest.

Phosphorus Ligand Substitution in Manganese and Rhenium Carbonyl-BETS Radical Complexes. When an organophosphorus ligand was added to a toluene solution containing either Mn or Re carbonyl-BETS radical complexes, a thermal substitution reaction took place and the daughter radical complex containing the additional ³¹P splitting was observed (Figures 3 and 4). Their ESR parameters are listed in Table II. For the majority of organophosphorus ligands, only monosubstitution was observed. However, a disubstitution was observed with trimethyl phosphite. Disubstitution of trialkyl phosphite

(13) Lionel, T.; Morton, J. R.; Preston, K. F. *J. Chem. Phys.* 1982, 76, 234.

(14) Note Added in Proof: The ¹³C hyperfine splitting assignment on the iron complex VII was suggested by A. Hudson. We believe the assignment is for the two ¹³CO ligands in the axial position.

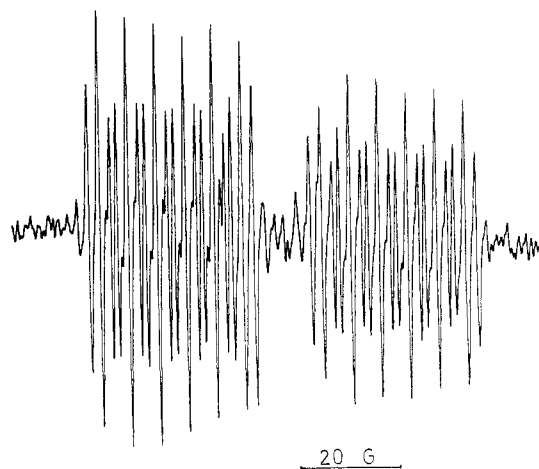


Figure 3. The ESR spectrum of Mn(CO)₃PPh₃-BETS radical complex in toluene at 23 °C.

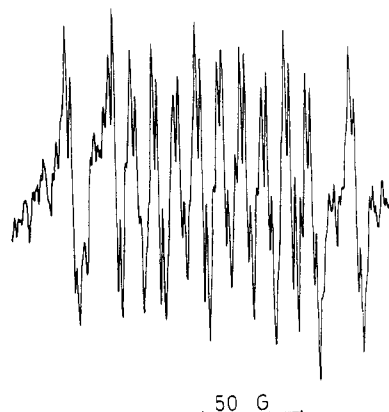


Figure 4. The ESR spectrum of Re(CO)₃PPh₃-BETS radical complex in toluene at 23 °C.

with metal-diketo radical complexes has been reported previously.^{2,9}

When an optically active DIOP ligand was used in substitution, the daughter radical complex became chiral. Currently we are assembling a custom circular dichroism spectrometer to examine the optical properties of these optically active metal-BETS radical complexes and their asymmetrical chemical reactions.

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Registry No. III (M = Mn), 91443-31-1; III (M = Re), 91443-32-2; VI, 91443-33-3; VII, 91443-34-4; Mn(CO)₃PPh₃-BETS, 91443-35-5; Re(CO)₃PPh₃-BETS, 91443-36-6.