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### ESR Investigation of the Rearrangement of a Heterobimetallic (Co/Mo) Dioxygen Complex. Characterization of a ·CN Free Radical

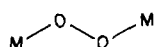
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A great number of dioxygen complexes of transition metals have been synthesized as either peroxy

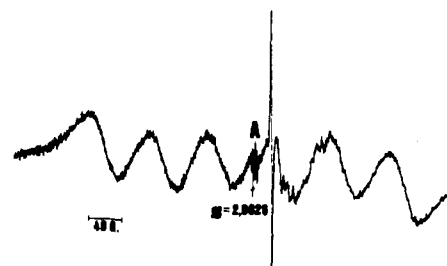
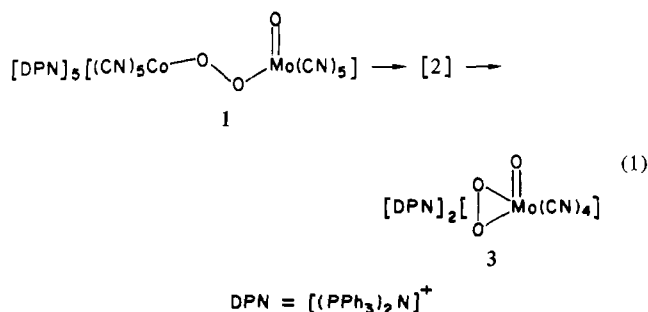


or  $\mu$ -peroxy

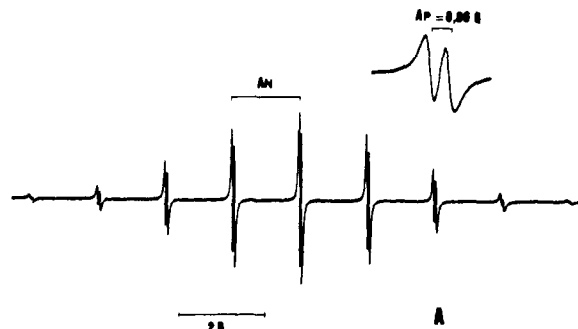


compounds.<sup>1</sup> The study of their reactivity has furthermore suggested that they are key intermediates in selective catalytic oxidations, when dioxygen is the oxidizing agent.<sup>2</sup> Many homogeneous<sup>3</sup> or heterogeneous<sup>4</sup> catalytic autoxidation processes, however, involve more than one type of metal. This led us to synthesize a heterobimetallic dioxygen complex in order to study the transfer of the dioxygen moiety from one metal center to the other in a multistep activation<sup>5</sup> of O<sub>2</sub>.

In the course of a study<sup>6</sup> of the rearrangement of such a complex (Co/Mo), an oxygen-18 labeling experiment suggested strongly the intermediacy of a molybdenum(V) compound<sup>7</sup> (2) able to react directly with dioxygen (eq 1).



**Figure 1.** ESR signal obtained by reacting compound 1 with dioxygen in CH<sub>2</sub>Cl<sub>2</sub>.



**Figure 2.** ESR signal of TCNE<sup>-</sup> (A in Figure 1) showing a small phosphorus splitting from the bis(triphenylphosphine)nitrogen(1+) cation.

The importance of this unprecedented observation brought us to investigate its mechanism by carrying out an ESR investigation.

### Experimental Section

Bis(triphenylphosphine)nitrogen(1+) ( $\mu$ -peroxy)pentacyanocobaltate(III) oxoquoopentacyanomolybdate(VI) (1) and bis(triphenylphosphine)nitrogen(1+) oxoperoxotetracyanomolybdate(VI) (3) were prepared as reported.<sup>6,7</sup> All solvents were reagent grade and thoroughly dried and degassed prior to use.

The ESR spectra were obtained on an X-band Varian Model E 109 spectrometer, at 25 °C with a cavity frequency of 8.9 GHz. The field was 3200 G, and the cavity of the spectrometer is a E.238 T M<sub>110</sub>.

The sample solutions were prepared with solvents thoroughly degassed on a vacuum line. Oxygen was introduced when it was desired by opening the system to air or pure oxygen atmosphere.

Thermolysis of *tert*-butyl peroxalate (*t*-BuOOCO)<sub>2</sub> was used to produce *tert*-butoxyl radicals during the generation of the "authentic" nitroxide 7.

### Results and Discussion

A methylene chloride solution of complex 1 in a strictly oxygen-free atmosphere shows no significant ESR signals even for long periods of time.

When the green solution is allowed to get in contact with air or oxygen, it becomes yellow and exhibits the ESR signals presented in Figure 1. The six broad bands ( $A_X = 70$  G,  $g \approx 2.0026$ ) characteristics of the coupling of the unpaired electron with a spin <sup>5</sup>/<sub>2</sub> nucleus cannot be unambiguously assigned.<sup>8</sup>

- (1) Vaska, L. *Acc. Chem. Res.* **1976**, *9*, 175-183.
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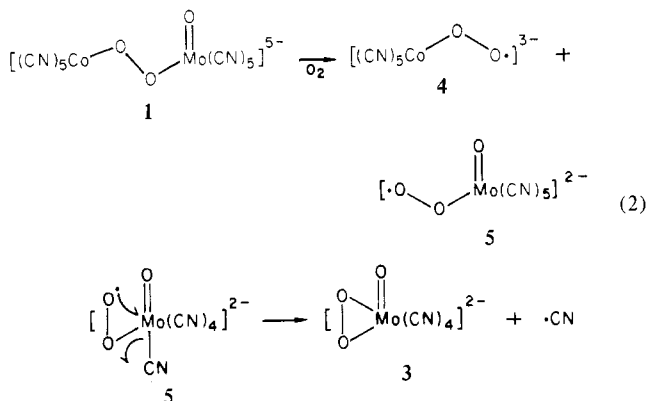
On the other hand, the signal (A) with approximately the same  $g$  value increased quickly in intensity and showed a pattern of nine main lines shown in Figure 2. The number of lines and their relative intensities (1/4/10/16/19/16/10/4/1) are characteristic of coupling of an unpaired spin density with four equivalent nitrogens. Furthermore, the magnitude of the coupling constant and the  $g$  value ( $A_N = 1.57$  G,  $g \approx 2.0026$ ) led us to assign this signal to the tetracyanoethylene radical anion (TCNE $^-$ ),<sup>10</sup> probably associated with the bis(triphenylphosphine)nitrogen(1+) cation. This was confirmed by the detection of a very small phosphorus hyperfine splitting ( $A_P = 0.06$  G) as shown in Figure 2.

This unexpected result implies the involvement of the solvent (CH<sub>2</sub>Cl<sub>2</sub>) in a side reaction during the rearrangement of **1** since, when the same reaction was performed in Et<sub>2</sub>O or CH<sub>3</sub>CN, **3** was equally formed, but without appearance of the nine-line signal.

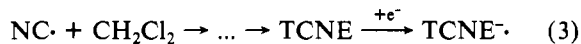
In order to prove that CH<sub>2</sub>Cl<sub>2</sub> was a true precursor of TCNE $^-$ , the rearrangement of **1** into **3** was carried out in <sup>13</sup>C-labeled methylene chloride.

Under identical experimental conditions the spectrum shown in Figure 3a was obtained. It corresponds to a mixture of TCNE $^-$  with an isomeric distribution in agreement with the enrichment of the starting methylene chloride. The simulation shown in Figure 3b was obtained with the following set of coupling constants:<sup>11</sup>  $A_N = 1.56$  G,  $A_{^{13}C_a} = 6.24$  G,  $A_{^{13}C_b} = 9.26$  G.

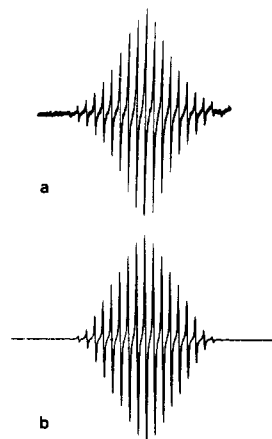
The results could be accounted for by the direct reaction of dioxygen with the molybdenum moiety (most probably via a molybdenum superoxo species **5**) followed by an intramolecular homolytic substitution to give the peroxomolybdenum complex **3** and the formation of cyano free radicals (eq 2).



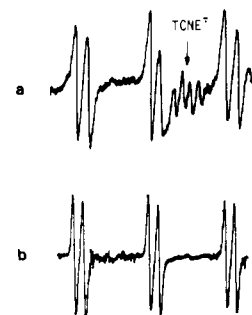
Tetracyanoethylene should then be formed by a complex sequence including reaction of  $\cdot\text{CN}$  with CH<sub>2</sub>Cl<sub>2</sub>, probably through the intermediacy of carbenic species<sup>12</sup> (eq 3).



- (8) The broad six-line spectrum cannot be assigned to a molybdenum species since the intense single line expected for all molybdenum isotopes with zero spin is missing. They could be attributed to Mn<sup>2+</sup> impurities. The cobalt superoxo complex **4** was not observed by ESR under the experimental conditions.<sup>9</sup>
- (9) Hoffmann, B. M.; Diemente, D. L.; Basolo, F. *J. Am. Chem. Soc.* **1970**, *92*, 61.
- (10) Rieger, R. H.; Bernal, I.; Reimuth, W. H.; Fraenken, G. K. *J. Am. Chem. Soc.* **1963**, *85*, 683.
- (11) A discrepancy exists between our value for  $A_{^{13}C_a}$  and that tentatively assigned by Rieger et al.<sup>10</sup>

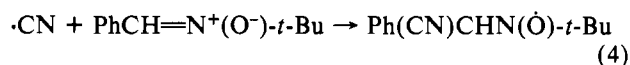


**Figure 3.** (a) ESR signal of TCNE $^-$  obtained by reacting compound **1** with dioxygen in <sup>13</sup>CH<sub>2</sub>Cl<sub>2</sub> (90% enriched). (b) Simulated spectrum with the following distribution ( $[(\text{CN})_2\text{C}^1=\text{C}^2(\text{C}^3\text{N})\text{CN}]^-$ ): C<sub>1</sub>\*-C<sub>2</sub>\*-C<sub>3</sub>, 77.4%; C<sub>1</sub>\*-C<sub>2</sub>\*-C<sub>3</sub>\*, 3.6%; C<sub>1</sub>\*-C<sub>2</sub>-C<sub>3</sub>\*, 0.8%; C<sub>1</sub>\*-C<sub>2</sub>-C<sub>3</sub>, 17.2%; C<sub>1</sub>-C<sub>2</sub>-C<sub>3</sub>, 1%.  $A_N = 1.56$  G,  $A_{^{13}C_a} = 6.24$  G, and  $A_{^{13}C_b} = 9.36$  G; the Lorentzian line width was 0.2 G.

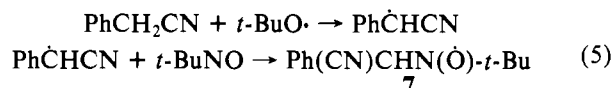


**Figure 4.** ESR signal of (a) Ph(CN)CHN(O)-*t*-Bu obtained by reacting compound **1** with dioxygen in the presence of PhCH=N<sup>+</sup>(O<sup>-</sup>)-*t*-Bu (reaction 4) and (b) PhCHN(O)-*t*-Bu obtained as described in reaction 5.

In order to support the intermediacy of  $\cdot\text{CN}$ , a spin-trapping experiment<sup>13</sup> was performed. The reaction of molecular oxygen with **1** was followed by ESR in the presence of phenyl *tert*-butyl nitron, PhCH=N<sup>+</sup>(O<sup>-</sup>)-*t*-Bu, which is a routinely used free-radical scavenger. A triplet of doublets ( $A_N = 15.0$  G,  $A_H = 2.0$  G,  $g = 2.0057$ ) was observed and assigned to nitroxide **7** (Figure 4a):



Our assignment was confirmed by producing **7** by the independent route shown in eq 5 (Figure 4b).



- (12) When Et<sub>2</sub>O or CH<sub>3</sub>CN were used, no species such as Co(CN)<sub>6</sub><sup>3-</sup> or cyanogen could be detected; hydrogen abstraction from the solvent should be the most plausible reaction of  $\cdot\text{CN}$  although we have no direct evidence for this.
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