Contribution from the Institute of Organic Chemystry and Institute of Physics,Polish Academy of Sciences, Warsaw, Poland

Electron Spin Resonance Studies of the Reaction Product Between Hydridodinitrogentris-(triphenylphosphine)cobalt(I) and Olefins. I.

S. Tyrlik, K. Falkowski, and K. Leibler

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During the reaction of hybridodinitrogentris(triphenylphosphine)cobalt(I) with styrenes a paramagnetic cobalt complex is formed. The ESR spectrum of this complex is believed to contains 15 hf lines. On the grounds of the chemical reactivity of the compound and computer analysis of its ESR spectrum it is shown to be a binuclear cobalt complex. The influence of different Lewis bases, protic substances and cobalt oxidation reagents on ESR spectra is reported.

Introduction

Hydridodinitrogentris(triphenylphosphine)cobalt(I), $(PPh_3)_3CoN_2H$. ether (I) reacts with cyclopentadiene giving a stable, diamagnetic complex of formula $(PPh_3)_3CoC_5H_5$.[1] Reaction with butadiene at low temperatures affords diamagnetic:[1]

$$PPh_3Co(\pi{-}C_4H_6)(\pi{-}C_4H_7)$$

Several reactions of olefins catalyzed by (I) or by complexes for which (I) is a direct precursor were also reported.[2] It is not mentioned that in those reactions paramagnetic cobalt species were synthetized. In the reaction of (I) with styrenes paramagnetic cobalt species are formed.

We intend to present here an analysis of the ESR spectrum and draw conclusions concerning the source of the paramagnetism observed.

Results and Discussion

Reactions of (I) with styrenes of formula:

$$RC_6H_4CH{=}CH_2;\ R{=}H;\ CH_3;\ OCH_3$$

(styrenes with substituents in para position were taken) in benzene solution with small molar ratio of (I): styrene = 1:0.4 to 1:2 gives a paramagnetic substance which has the same ESR spectrum as the above listed styrenes. This spectrum is presented in Figure 1. The ESR signal appears several seconds after styrene has been added to the solution of (I) in benzene. The temperature and concentration conditions were as indicated in Figure 1.

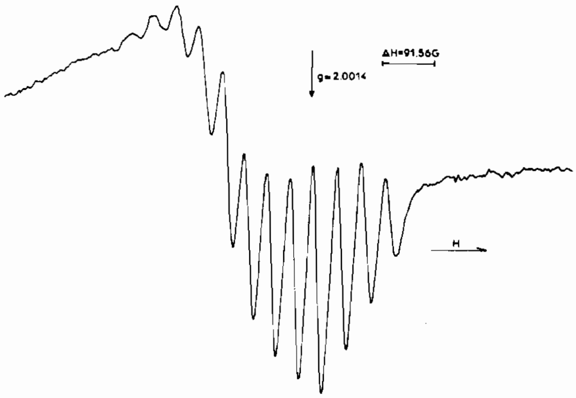

Figure 1. ESR spectrum of the reaction mixture of (I)+ $PhCH{=}CH_2{=}1{:}0.5$; $c_{Co}{=}0.014\ M$; temp. 25°C; temperature of the cavity 20°C.

The same spectrum is observed during interaction of (I) with the trimethylaluminium dimer Al_2Me_6. Both reactions mentioned proceed according to equations:

$$(I)+PhCH{=}CH_2\xrightarrow{\text{benzene}}(II)+PhCH_2CH_3+N_2 \qquad (1)$$

$$(II)+Al_2Me_6\xrightarrow{\text{benzene}}(IIA)+CH_4+C_2H_6+N_2+\text{products of } Al_2Me_6 \text{ decomposition} \qquad (2)$$

Reaction mixture (1) contains unreacted $PhCH = CH_2$ [even in the presence of an excess of (I)], unreacted (I), the paramagnetic reaction product (II) and ethylbenzene. Ethylbenzene is present in an amount of 5% of styrene (in the reaction conditions as indicated in Figure 1). We do not know the quantity of the parent complex (I) which has been converted; so we cannot give the precise yield of ethylbenezene relative to the cobalt complex. In order to obtain a complete reaction of (I) there should be an excess of about 8 to 10 moles of styrene as compared with (I). In that case the spectrum of the

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[1] P.V. Rinze, Zur Chemie der Kobalt-Stickstoff Komplexe and zur Darstellung von Kobalt (I) - Organyl Verbindungen. Thesis, Philipps Universität, Marburg/Lahn 1970.
[2] A. Yamamoto, S. Kitazume, Lyong Sun Pu, S. Ikeda, *J. Am. Chem. Soc.*, 93, 371 (1971).

reaction solution appears as in Figure 2. A very similar spectrum to those presented in Figure 2 was obtained after having the reaction mixture to stand for 12 hours (for the molar ratio 1:1). There is a gradual disappearance of the hyperfine structure with time.

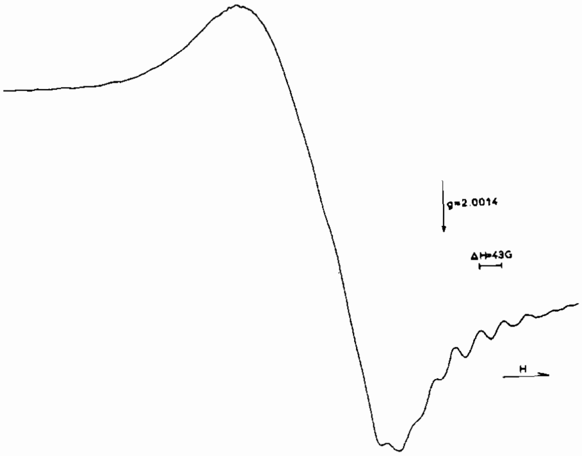


Figure 2. ESR spectrum of the reaction mixture of (I)+ PhCH=CH$_2$=1:0.5; c_{Co}=0.015 *M*; temp. 25°C.

Benzene solution after reaction (2) performed with a 1:2 molar ratio of (I): Al$_2$Me$_6$ contains paramagnetic substance (IIA), products of Al$_2$Me$_6$ decomposition, but does not contain (I). This has been proved by the disappearance of the ν(N$_2$) band and the evolution of N$_2$ with an about 95% yield. The gases evolved contain about 50% of N$_2$, 40% of methane and small amounts of ethane. The yield of CH$_4$ relative to the parent complex was about 10%. We cannot decide at present if there are other cobalt-containing diamagnetic products of the reaction (1) and (2).

The IR spectrum of reaction solution (1) for small molar ratios (I): styrene can be interpreted as superimposed spectra of (I), styrene and ethylbenzene. In high molar ratios ν(N$_2$) disappears and the bands attributable to PhCH=CH$_2$ increase.

The ESR spectrum presented in Figure 1 consists of 12 well resolved lines but as it will be shown later the real number of lines is 15. If a paramagnetic product (II) should be a mononuclear cobalt complex it should have 8 lines, since the common isotope of cobalt (^{59}Co, 100% abundance) has a nuclear spin I = 7/2. If the electron spends an equal amounts of time on either cobalt atom a and b one would expect to find

$$2(I_a+I_b)+1=15 \text{ lines}$$

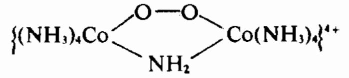
If the electron spends more time on one cobalt than on the other, one would expect

$$(2I_a+1)(2I_b+1)=64 \text{ lines}$$

The fact that no additional splittings have been seen shows that the unpaired electron density on any ligand must be very low.

The evident asymmetry of the spectra can be interpreted according to Ebsworth and Weil[3] who investigated binuclear cobalt complexes of the formula:

$$\{(NH_3)_5{-}Co{-}O{-}O{-}Co(NH_3)_5\}^{5+}$$



ESR spectra are described by a conventional spin Hamiltonian which contains electronic Zeeman terms as well as a hyperfine interaction term with two cobalt nuclei:

$$H = g\beta HS + ASI$$

According to this Hamiltonian, a Zeeman transition is split into hyperfine components, the number of which depends on a projection of the total spin on the axis of quantization.

The spacings between the hyperfine lines are the same over the whole spectrum - so we can deduce than both cobalt nuclei are magnetically equivalent. The spectrum should consist of 15 equally speced lines occurring at a magnetic field of

$$\frac{h\nu - A\sum_{j=1}^{8} m_j}{g\beta}$$

where m_j is the projection of the total nuclear spin (the sum of spins of two cobalt nuclei) on the quantization axis.

In order to explain the asymmetrical shape of the entire spectrum and the experimentally observed numberber of components we performed a computer simulation of the spectrum. The simulated spectrum consists of 15 equally spaced lines with an intensity distribution:

1:2:3:4:5:6:7:8:9:8:7:6:5:4:3:2:1

which is proper for two cobalt nuclei with a nuclear spin I = 7/2.

We tried to explain the spectrum by the hypothesis that line widths of individual components are functions of quantum number m_j. For a Gaussian line shape the total spectrum may be written as[3]

$$f(x)= \sum_{m=-7}^{m=+7}(8-|m|)\frac{x+md}{(c_o+mc)^2}\exp[\frac{(x+md)^2}{(c_o+mc)^4}\}$$

where x is proportional to the magnetic field H; d is the spacing between the hf lines and $2(c_o+mc)^2$ is the width between the points of a maximum slope of the Gaussian line; c is a parameter which (following Ebsworth and Weil[3]) describes the change of the line width m_j, and thus the asymmetry of the entire spectrum.

The same procedure was performed for the Lorentzian function where the line shape may be written as

$$f(x)= \sum_{m=-7}^{m=+7}(8-|m|)\frac{x+md}{(c_o+mc)^2}\{3+4[\frac{x+md}{(c_o+mc)^2}]^2\}^{-1}$$

with the same meaning of the parameters as for the Gaussian shape.

The simulated spectra for both the line shapes for d = 42.0 G are presented in Figure 3 and 4. We have found that in both cases there is a set of parameters which describes the total line shape quite well. The existing discrepancies are due to the fact that the true line shape should be described by a more complicated function, a combination of Gaussian and Lorentzian line shapes. From the inspection of the calculated curves it is evident that in the outer parts of the experimental spectrum the line shape is more Lorentzian than Gaussian.

The overall agreement of observed and calculated line shapes supporte the hypothesis of the dependence of the line width on I_z.

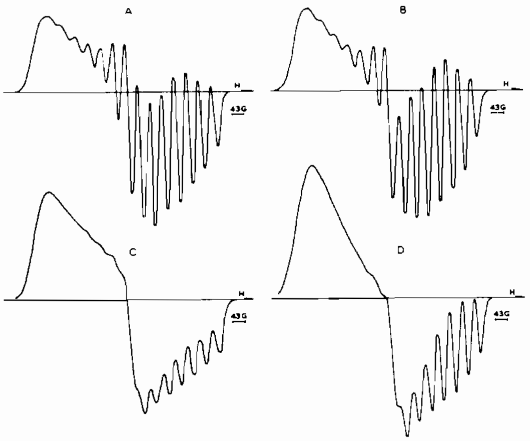


Figure 3. Calculated Lorentzian line shapes with spacing d=42.0 G with

A) c=0.06 c_o=2.7
B) c=0.07 c_o=2.7
C) c=0.06 c_o=3.0
D) c=0.10 c_o=3.0

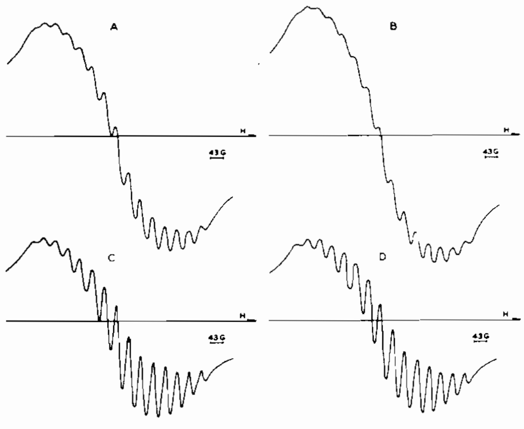


Figure 4. Calculated Gaussian line shapes with spacing d=42.0G with

A) c=0.07 c_o=2.50
B) c=0.07 c_o=2.70
C) c=0.10 c_o=2.00
D) c=0.07 c_o=2.00

The observed anisotropy shows that the line width should increase with the increasing g factor. This effect was explained by McConnell and McGarvey for copper compounds[4,5] and by McGarvey[6] for Ti^{3+}, V^{4+}, Mn^{6+}, Mn^{2+}, Fe^{3+}.

The results obtained clearly indicate that there are 15 components in the entire line. At the low field end of the spectrum the overlapping of the lines is such that it leads to a partial cancellation of the absolute intensities of the components.

Thus, the paramagnetic substance (II) should be a bicobalt species. All attempts to isolate this product were unsuccesful.

We have been also unable to isolate the paramagnetic substance (IIA) in spite of numerous attempts. Both paramagnetic substances (II) and (IIA) are probably identical in structure.

Reactions of other olefins like pentene-1, hexene-1 etc. does not produce any paramagnetic substance (in analogous conditions). In that case we have not observed hydrogenation products. The consumption of hydridic hydrogen in reactions (1) and (2) and lack of hydrogenation products during interaction of (I) with ethylenes substituted with aliphatic radicals leads to the conclusion that the appearance of paramagnetic complexes is connected with the homolytic rupture of the Co-H bond. It was interesting to know if a paramagnetic substance (II) contains a hydridic hydrogen. To elucidate this question we performed a reaction with CCl_4 of the reaction mixture (1) prepared with molar ratio (I): styrene = 1:8 (that is in conditions when the parent (I) was completely consumed). No chloroform was detected. This observation excludes the structure for

$$L_3Co^{1+}H \ldots L_xCo^0;\ x=2 \text{ or } 3;\ L=PPh_3$$

paramagnetic substance (II).

Another argument against the presence of hydridic hydrogen in paramagnetic substance (II) is the lack of hyperfine structure which could be ascribed to the coupling of an unpaired electron with ^1H.

Reaction with CCl_4 affords the $(PPh_3)CoCl_2$ with almost quantitative yield. This observation indicates that cobalt in (II) is in a low oxidation state. CCl_4 is known as oxidizing agent for cobalt compounds in reduced state.[7] When $CHCl_3$ is gradually added to the reaction mixture the signal changes (Fig. 5). The hyperfine structure disappears already when the molar ratio total cobalt: $CHCl_3$ = 1:0.16. This observation indicates that the quantity of paramagnetic cobalt atoms is about 16% of total cobalt. After addition of $CHCl_3$ in the proportion Co: $CHCl_3$ = 1:3, the compound $(PPh_3)_2CoCl_2$ was also isolated.

We cannot distinguish, at present, between the structures $[L_xCo^{1+} \ldots L_xCo^\circ]^{\cdot +}$ $[L_xCo^{-1} \ldots L_xCo^\circ]^{\cdot -}$; x = 2 or 3 for paramagnetic substances (II) and (IIA). Biradical structure $[L_xCo^\circ \ldots L_xCo^\circ]^{\cdot\cdot}$ is not very probable. The reaction with $CHCl_3$ together with the fact that precision of spin quantity measurements is low precludes the use of the spin quantity as an argument against or for biradical structure.

We considered also the possibility of existence in

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(3) E.A.V. Ebsworth, J.A. Weil, *J. Phys. Chem.*, 63, 1890 (1959).
(4) H.M. Mc Connel, *Connel, J. Chem. Phys.*, 25, 709 (1956).
(5) B.R. Mc Garvey, *J. Phys. Chem.*, 60, 71 (1956).
(6) B.R. Mc Garvey, *J. Phys. Chem.*, 61, 1232 (1957).
(7) A. Sacco, M. Rossi, *Inorg. Chim. Acta*, 2, 127 (1968).

(II) of « microcrystallites » with two or more magnetically non-equivalent cobalt nuclei. This model should give rise to two groups of 8 hf lines in slightly different positions. However, good agreement of calculated and observed spectra favours the former model.

It was interesting to know the influence of various reactants on the ESR spectrum of a dicobalt complex (II).

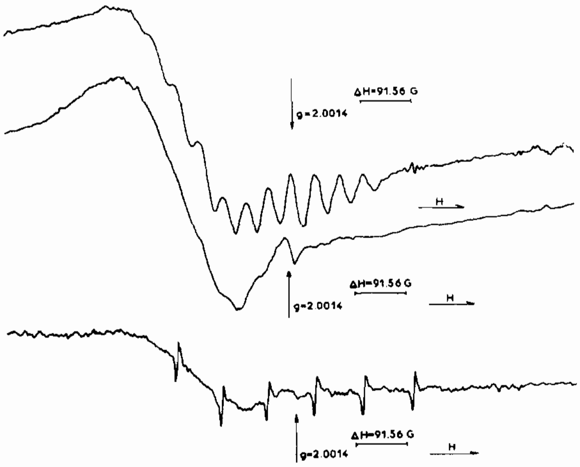

Figure 5. ESR spectrum of the reaction mixture of (I)+ PhCH=CH$_2$=1:1+CHCl$_3$

upper curve	total C: CHCl$_3$ = 1:0.08
middle curve	= 1:016
lower curve	= 1:0.8

On this curve the manganese field marker is recorder. Other conditions as in Fig. 1.

Reactions with CN-containing ligands. Vinyl cyanide causes the disappearance of the hyperfine structure as shown in Figure 6.

Tetracyanothylene during interaction with (II) gives a substance which exhibits an ESR spectrum presented in Figure 7. This nine-line spectrum indicates that the unpaired electron interacts equally with the four nitrogen atoms. Nitrogen Complex (I) itself does not react with tetracyanoethylene giving a paramagnetic complex with nine-line structure.

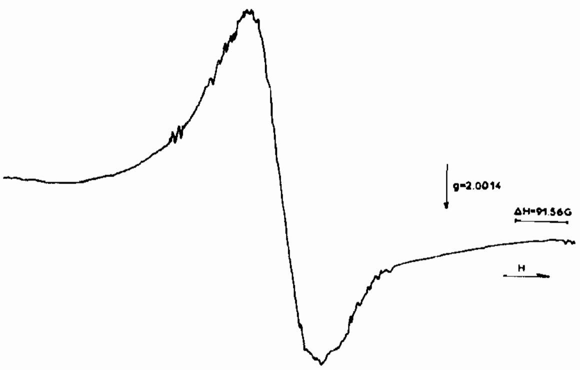

Figure 6. ESR spectrum of the reaction mixture of (I)+ PhCH=CH$_2$ = 1:1 + vinyl cyanide. Other conditions as in Fig. 1.

Reaction of a solution containing (II) with another strong acceptor 1.3.5-trinitrobenzene causes the disappearance of the signal.

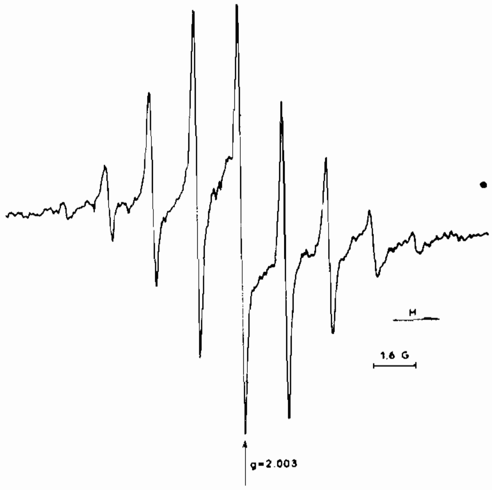

Figure 7. ESR spectrum of the reaction mixture (I)+PhCH= =CH$_2$ = 1:1 + tetracyanoethylene. Cobalt: TCNE + 1:0.5. Other conditions as in Fig. 1.

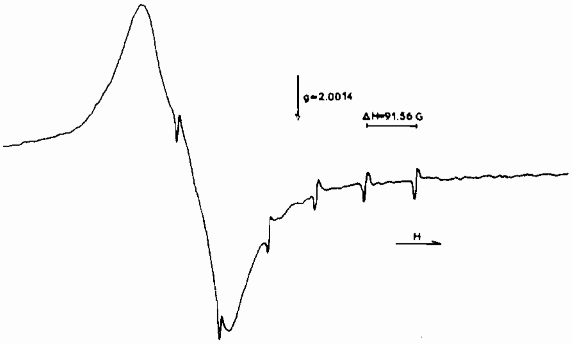

Figure 8. ESR spectrum of the reaction mixture (I): PhCH= =CH$_2$ = 1:1 + triethylphosphine. The six peaks seen come from the manganese field marker. Other conditions as in Fig. 1.

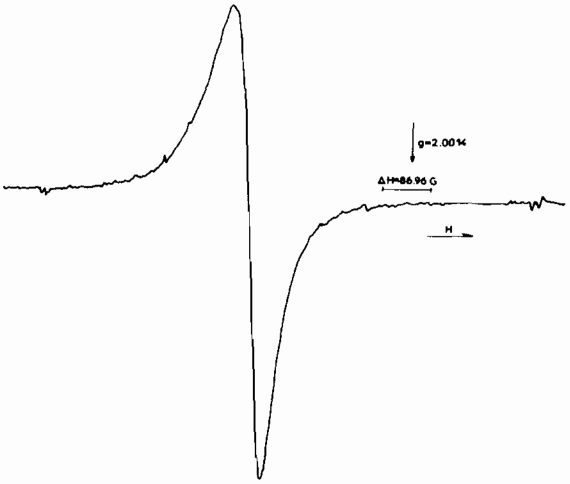

Figure 9. ESR spectrum of the reaction mixture (I): PhCH=CH$_2$ = 1:1 + DMSO. Other conditions as in Fig. 1.

Reactions with other Lewis bases. Tertiary amines have no influence on the spectrum presented in Figure1. Triethylphosphine and DMSO coordinates to the dicobalt complex causing disappearance of the hyperfine structure and narrowing of the spectrum as shown in Figure 8 and 9. On the contrary, coordination of $P(OCH_3)_3$ produces a complex with more complicated hyperfine structure as shown in Figure 10.

Reactions with acidic hydrogen. Mineral and organic acids cause a very fast disappearance of the ESR signal. The signal disappears within several minutes after acetylacetone and alcohols: methanol, ethanol and Ph_3COH, have been added.

Reactions with other olefins. The solution after reaction (1) does not exhibit any changes in the shape of the signal when aliphatic olefins with a double bond in position 1 or 2 have been added. There is also no change with cyclic olefins like cyclohexene or cyclooctene.

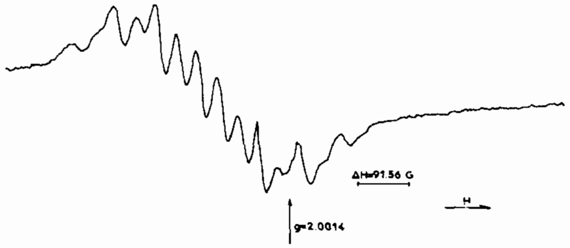

Figure 10. ESR spectrum of the reaction mixture (I): Ph-$CH=CH_2$ = 1:1 + trimethlylphosphite. Other conditions as in Fig. 1.

Experimental

Hydridodinitrogentris(triphenylphosphine)cobalt (I) was synthetized according to the Yamamoto method.[2] Cobaltous acetylacetonate used in this procedure was synthetized in the usual way.[8] Triisobutylaluminum and triphenylphosphine used was reagent grade, without further purification. All operations were performed under prepurified (over BTS catalyst) nitrogen and with deoxygenated solvents. Solutions of (I) were siphoned to avoid the use of syringes. Only the organoaluminium compound and solutions of reactants in small volumes (up to 1 ml) were added by syringes. ESR tubes were always flushed with prepurified nitrogen.

All further reactions of the reaction mixture (1) were carried out with a 1:2 molar ratio of the total cobalt present in the reaction (1) to the remaining substrates listed in captions. An exception to this molar ratio were the reactions with TCNE 1:0.5 and with $CHCl_3$ molar ratios indicated in the Fig. 5. The 230-232°C (decomp.). Samples of the reaction mixture were hydrolyzed with PhCOOH and evaporated under vacuum at room temperature. Vapours condensed in –80°C were analyzed in a gas chromatopgraph CHROMATOPREP N–502 with 1–m columm of 3% SE30 on chromosorbe P at 70°C. The hydrocarbons evolved during reaction (2) were analysed on the same apparatus with 3–m column of 20% glycol solution of $AgNO_3$ on choromosorb P at room temperature. In both cases a flame detector was used with argon as a carrier gas. Hydrogenation products in reaction (1) were also detected without hydrolysis by evaporating the reaction solution and analysing vapours. Analysis for chloroform was carried out, after evaporation on a Perkin-Elmer gas chromatograph with Katharometer detector. A column composed of 2 m carbowax 400 (10% on chromosorb P) and 1–m polypropyleneglycol (15% on chromosorb P) was used at 42°C with hydrogen as carrier gas. ESR spectra were measured on JEOL JM 3X spectrometer. The cavity temperature was 20°C. The spectra were simulated with an ODRA 1013 computer.

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(8) B.E. Bryant. W.C. Pernelius, in *Inorg. Synth.*, 5, 188, ed. Mc Graw Hill Book Comp. New York 1957.