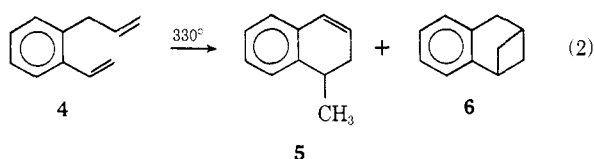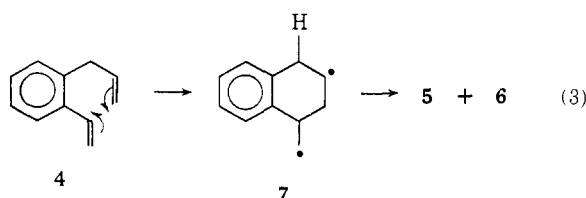similar reaction conditions (330°, 13 hr). Complete conversion was observed to 1-methyl-1,2-dihydronaphthalene (5, 90-95%) and benzonorpinene (6, 5-8%) (eq 2). In addition, about 1% of another ene

product, benzocyclohepta-1,3-diene, was detected. All products were independently subjected to the pyrolysis conditions and found to be stable.

Only a few examples of intramolecular cycloaddition of double bonds (6) have been previously reported.[6] Although the dihydronaphthalene 5 can be produced through a concerted ene mechanism, the norpinene 6 requires a diradical process. The double bonds react to give the diradical 7, which can either collapse to form 6 or undergo a hydrogen shift to complete the ene reaction that forms 5 (eq 3). A continuum of mech-

anisms is possible for an ene reaction, ranging from rate-determining formation of a diradical by double-bond–double-bond addition, through a concerted process, to rate-determining abstraction of the allylic hydrogen.[1] The most favorable transition state for the concerted process has the planes of the double bond (the enophile) and of the allylic system (the ene) parallel and the allylic carbon–hydrogen bond parallel to the adjacent π orbitals.[7] Because this arrangement is difficult or impossible to realize in 4, the reaction occurs by direct closure of the closely situated double bonds to form the diradical 7. Cyclobutane ring formation has been cited previously as evidence for a diradical ene mechanism.[3] The longer side chains offered by 1 permit the optimal arrangement for a concerted ene process. As a result, no cyclobutane product is observed.

To summarize, we have found that intramolecular ene reactions occur very readily between ortho side chains of benzene rings, because the reactive components are constrained close to each other. The reaction mechanism, however, can vary from what is probably a concerted process when the chains are sufficiently long, to a diradical process in shorter chains when full overlap of all the necessary orbitals is not possible.

(6) For a list of such examples, see J. Meinwald and J. A. Kapecki, *J. Amer. Chem. Soc.*, 94, 6235 (1972); S. F. Nelson and J. P. Gillespie, *ibid.*, 94, 6238 (1972). The structure of 6 followed from its mass spectrum (parent peak same as 4) and nmr spectrum (no alkenic protons). Its spectra were quite different from those reported for the other possible cycloaddition product, benzobicyclo[3.2.0]heptene.

(7) See structure 122 in ref 1.

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Stereochemically Nonrigid Ruthenium(III) and Cobalt(III) Tris-Chelate Complexes

Sir:

We report here preliminary results of a proton magnetic resonance (pmr) investigation of stereochemically nonrigid tris(dithiocarbamato)ruthenium(III) and -cobalt(III) complexes. Tris(N,N-methylbenzyldithiocarbamato)ruthenium(III), Ru(MeBzdtc)$_3$, and tris(N,N-dibenzyldithiocarbamato)cobalt(III), Co(BzBzdtc)$_3$, have been synthesized[1] and their pmr spectra[2] recorded from -40 to $+70°$ in CD$_2$Cl$_2$ (Figure 1) and 30 to 200° in NO$_2$C$_6$D$_5$ (Figure 2), respectively. Both complexes are stereochemically nonrigid on the pmr time scale. For Co(BzBzdtc)$_3$ the coalescence is due to intramolecular metal centered inversion ($\Lambda \rightleftarrows \Delta$), and for Ru-(MeBzdtc)$_3$ the low-temperature coalescence (*ca.* -13 to $+43°$) also results from $\Lambda \rightleftarrows \Delta$ inversion while the high-temperature coalescence (*ca.* 43-64°) is due to S$_2$C–N bond rotation (*vide infra*). Ru(MeBzdtc)$_3$ is the first tris-chelate complex of ruthenium found to be nonrigid, indeed the only other ruthenium compounds reported to date which are nonrigid with respect to metal centered rearrangement are of the type H$_2$RuL$_4$[3] and HRu(PF$_3$)$_4^-$[4] where L is a phosphine or phosphite. Co(BzBzdtc)$_3$ is only the second tris-chelate complex of cobalt(III) found to be nonrigid with respect to inversion on the pmr time scale. The other, tris(α-R-tropolonato)cobalt(III), where R = isopropyl or isopropenyl, was recently reported.[5]

Ru(MeBzdtc)$_3$ is paramagnetic with μ_{eff} = 1.88 BM in the solid at 23°. This places the complex in the low-spin d^5 category which is the same as other Ru(dtc)$_3$ complexes (μ_{eff} = 1.74-1.88 BM).[1b] The compound is an unsymmetrical tris chelate and exists as a mixture of cis, C, and trans, T, isomers in solution. The pmr spectrum of the methyl group at $-35°$ consists of the four expected resonances which are labeled T$_1$, T$_2$, T$_3$, and C (Figure 1). The C resonance is identified because the C:T ratio is slightly less than statistical. The other seven lines are due to the methylene groups. Actually eight methylene resonances are expected but two are accidentally degenerate.[6] The eight resonances derive from the diastereotopic relationship between the CH$_2$ protons.[6] This spectrum requires that both metal-centered $\Lambda \rightleftarrows \Delta$ inversion and S$_2$C–N bond rotation are slow on the pmr time scale. The total spread of the methylene resonances is 15.4 ppm. This large chemical shift difference should be compared with the spread of *ca.* 0.5 ppm observed for diamagnetic Co-(MeBzdtc)$_3$[7] and results from the isotropic interaction.

(1) These complexes were synthesized according to published procedures: Co(BzBzdtc)$_3$, (a) L. M. Compin, *Bull. Soc. Chim. Fr.*, 27, 464 (1920); Ru(MeBzdtc)$_3$, (b) L. Malatesta, *Gazz. Chim. Ital.*, 68, 195 (1938). This ruthenium complex is new and was purified by column chromatography using silica gel and benzene eluent. Both complexes were characterized by elemental analysis and pmr and ir spectra.

(2) All pmr spectra were recorded with a Varian XL-100-15 nmr spectrometer operated in the ^{2}H locked mode.

(3) P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 92, 3482 (1970).

(4) P. Meakin, J. P. Jesson, F. N. Tebbe, and E. L. Muetterties, *ibid.*, 93, 1797 (1971).

(5) (a) S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *ibid.*, 94, 6411 (1972); (b) S. S. Eaton and R. H. Holm, *ibid.*, 93, 4913 (1971).

(6) Two resonances result from the cis isomer which has C$_3$ symmetry and six (three diastereotopic pairs) from the trans which has C$_1$ symmetry.
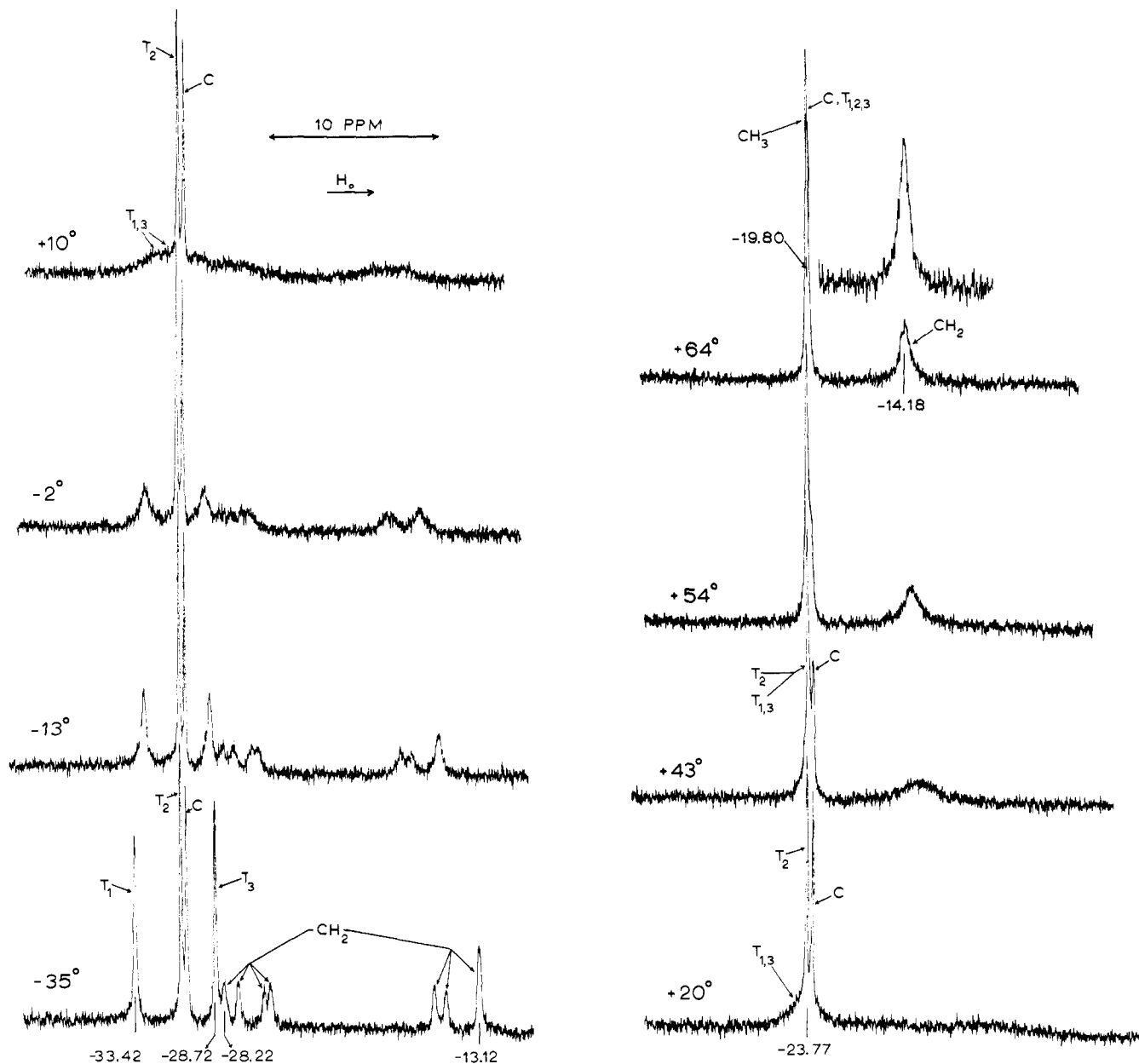
Figure 1. Pmr traces of the CH_3 and CH_2 region for $Ru(MeBzdtc)_3$ at various temperatures in CD_2Cl_2 solution recorded at 100 HHz. Chemical shifts are in ppm relative to $CHDCl_2$. Negative shifts are downfield.

This phenomenon often greatly simplifies stereochemical analyses of paramagnetic complexes.[8]

As the temperature is increased all of the CH_2 resonances simultaneously collapse (coalescence at ca. $+20°$) and two of the trans CH_3 resonances, T_1 and T_3, broaden and coalesce. The other CH_3 lines, T_2 and C, are *not* affected by this kinetic process which is complete on the pmr time scale at ca. $+40°$. The $+43°$ spectrum shows a broad CH_2 resonance and three CH_3 resonances, T_2, $T_{1,3}$, and C. The $T_{1,3}$ and T_2 resonances are accidentally degenerate. This kinetic process does not cause cis–trans isomerization and therefore cannot be $S_2C–N$ bond rotation. The coalescence pattern is identical with the one found for the low-temperature process of $[Fe(MeBzdtc)_3]BF_4$.[9] For this complex the process was unambiguously assigned as the stereochemical

rearrangement consistent with a trigonal-twist mechanism. This mechanism is illustrated in Figure 3 of ref 9. Several other unsymmetrical tris-chelate complexes[10] show identical methyl coalescence patterns with that of $Ru(MeBzdtc)_3$. The rearrangement mechanism in these has also been assigned as a trigonal twist.[11] The CH_2 averaging pattern shows that the $T_1 \rightleftarrows T_3$ environmental averaging is accompanied by $\Lambda \rightleftarrows \Delta$ inversion. All four diastereotopic pairs coalesce. The trigonal-twist mechanism requires that

(7) T. H. Siddall, III, *Inorg. Nucl. Chem. Lett.*, 7, 545 (1971).
(8) R. H. Holm, *Accounts Chem. Res.*, 2, 307 (1969).
(9) D. J. Duffy and L. H. Pignolet, *Inorg. Chem.*, 11, 2843 (1972).

(10) Fe(MePhdtc)₃: M. C. Palazzotto and L. H. Pignolet, *J. Chem. Soc., Chem. Commun.*, 6, (1972); and Co(α-C₃H₅-tropolonate)₃, ref 5.

(11) The trigonal-twist mechanism is envisioned as a twisting motion of one triangular face with respect to the other about the real- or pseudo-C_3 symmetry axis of the cis and trans isomers, respectively. The transition state is assumed to possess trigonal-prismatic geometry. This mechanism requires the observed environmental averagings but is by no means proved by these results. Indeed, only the stereochemical permutation is demonstrated; however, the trigonal-twist mechanism is the most reasonable pathway for this rearrangement.

eight CH_2 resonances simultaneously coalesce into four (2 in ref 9). In the $+43°$ spectrum of $Ru(MeBzdtc)_3$ these four lines are not resolved because S_2C-N bond rotation is beginning to average all of the resonances (*vide infra*). These qualitative pmr results clearly demonstrate that the low-temperature process in $Ru(MeBzdtc)_3$ results from a trigonal-twist mechanism.[12] The rate constant for $\Lambda \rightleftharpoons \Delta$ inversion *via* the trigonal-twist mechanism is *ca.* 78 $\sec^{-1}$ at $+10°$ and $\Delta F^{\mp} = 13$ kcal/mol.

The high-temperature coalescence which averages the remaining CH_3 and CH_2 resonances presumably results from S_2C-N bond rotation. A similar signal collapse with an almost identical coalescence temperature is observed with $Co(MeBzdtc)_3$ for which S_2C-N bond rotation is the only reasonable process. Ligand exchange also cannot account for any of the coalescences because a mixture of $Ru(MeBzdtc)_3$ and $Ru(MePhdtc)_3$ in CD_2Cl_2 showed no signs of mixed complexes after 5 hr at $+60°$.

$Co(BzBzdtc)_3$ is a symmetrical tris-chelate complex. In the limit of slow $\Lambda \rightleftharpoons \Delta$ optical inversion the diastereotopic methylene protons are nonequivalent. At $+120°$ inversion is slow and an AB pattern is observed with $\nu_A - \nu_B = 0.142$ ppm and $J = 15.3$ Hy. As the temperature is increased the AB pattern collapses into a single sharp line (Figure 2). The coalescence pattern has been simulated by a computer calculation assuming chemical exchange between environments A and B. The coalescence is not caused simply by the temperature dependence of the chemical shift. A computer simulation in which $\nu_A - \nu_B$ gradually approaches zero for nonexchanging nuclei does not fit the experimental coalescence pattern. At $168°$ the rate constant for exchange is 17.6 $\sec^{-1}$ yielding $\Delta F^{\mp}$ of 23.6 kcal/mol. The complex is completely stable at $200°$ and the pattern shown in Figure 2 is reversible and reproducible even after several days in solution. The process is intramolecular because ligand exchange is slow. A mixture of $Co(BzBzdtc)_3$ and $Co(MeBzdtc)_3$ showed no signs of mixed complexes after 24 hr.[15] No mechanistic information can be obtained from these results. It is probable that $Co(BzBzdtc)_3$ rearranges *via* the same mechanism as $Ru(MeBzdtc)_3$. Indeed, $Fe(dtc)_3$ and $[Fe(dtc)_3]BF_4$ complexes also rearrange by this mechanism.[16]

It is interesting to compare the relative rates of metal centered rearrangement for various complexes. Sev-

Figure 2. Pmr traces of the CH_2 region for $Co(BzBzdtc)_3$ at various temperatures in $NO_2C_6D_5$ solution recorded at 100 MHz.

eral reviews have recently been published.[17] Ru^{III}-(dtc) complexes have higher activation enthalpies than analogous Fe(III) complexes,[18] $\Delta H^{\mp} = $ *ca.* 13 and 9 kcal/mol, respectively. This is the same trend found for H_2FeL_4 and H_2RuL_4 where L = tertiary phosphine or phosphite.[3] $Co(BzBzdtc)_3$ rearranges faster than $Co(acac)_3$[19] but slower than $Co(\alpha-R-tropolonate)_3$;[5] $\Delta H^{\mp} = $ *ca.* 26, $E_a = 31–33$, and $\Delta H^{\mp} = 14–16$ kcal/mol, respectively. The dithiocarbamato and tropolonato complexes rearrange by a trigonal-twist mechanism while the substituted acetylacetonato complexes rearrange predominantly by bond rupture.[14,20]

It has been suggested[21] that the ground-state geometry has an influence on the rate and mechanism of stereochemical rearrangement. $Fe(MePhdtc)_3$[22] and $Co(EtEtdtc)_3$[23] have very similar ground-state geometries but $\Delta H^{\mp}$ differs by *ca.* 15 kcal/mol for analogous compounds (*vide supra*). The electronic configuration of the metal obviously has the largest effect on the rate of $\Lambda \rightleftharpoons \Delta$ inversion for these compounds.

(12) These results are sufficient to eliminate all other rearrangement modes. Discussions in ref 5, 9, 13, and 14 should be referred to for detailed arguments.

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(14) J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, 92, 5319 (1970).

(15) $Co(BzBzdtc)_3$ was also mixed with $Fe(MeMedtc)_3$ in $NO_2C_6D_5$ resulting in no mixed complexes after 5 hr at $+70°$.

(16) All of these complexes have been examined in the presence of their respective thiuram disulfides. The pmr spectra above the high-temperature coalescences show separate resonances for coordinated dtc and thiuram disulfide indicating that this compound does not enter into the rearrangement mechanism.
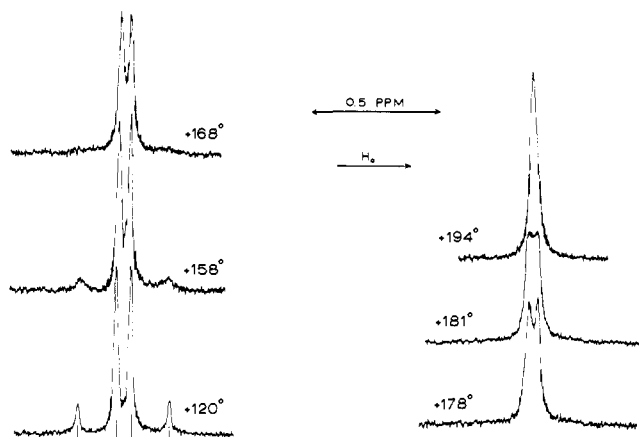
(17) N. Serpone and D. G. Bickley, *Progr. Inorg. Chem.*, in press; and J. J. Fortman and R. E. Sievers, *Coord. Chem. Rev.*, 6, 331 (1971).

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