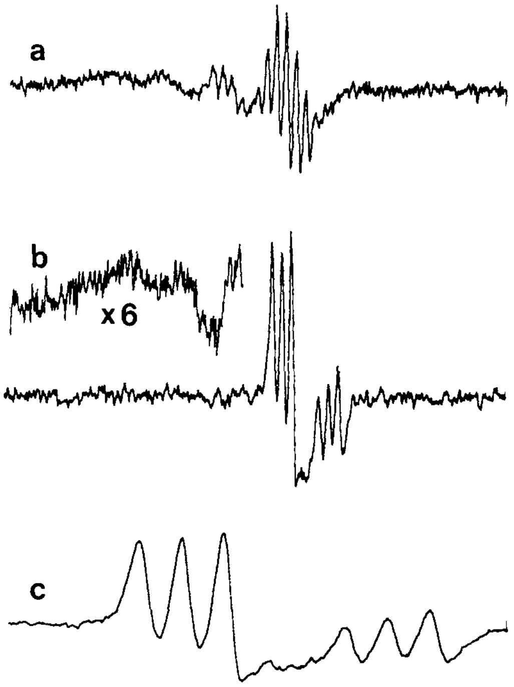

Figure 1. X-band EPR spectra of copper porphyrin complexes in $CHCl_3$ solution at ~21 °C: (a) copper porphyrin complex VI, 1000-G scan, (b) spin-labeled copper porphyrin complex, V, 1000-G scan, and (c) V, 200-G scan of nitroxyl region. All spectra were obtained at power levels well below saturation, using modulation amplitudes which did not cause observable broadening, on solutions sufficiently dilute that intermolecular exchange did not cause observable broadening.

broadened by incomplete motional averaging.[6] The EPR spectrum of the spin-labeled copper porphyrin V is substantially different from a superposition of the spectra of III and VII, exhibiting a doublet of triplets in the nitroxyl region and a greatly broadened copper spectrum. Integration of the spectrum relative to the spectra of III and VII indicates that the area is equivalent to two unpaired electrons. The splitting pattern in the nitroxyl region can be interpreted as an "AB"-type pattern (by analogy with NMR nomenclature[7]). The splitting between the two triplets is 77 G (0.0072 cm^{-1}). The g-value differences for copper porphyrin and nitroxyl correspond to a $\Delta g \approx 150$ G. Using the standard formulae for interpretation of AB spectra,[7] the intensities of the spectral components are predicted to be in the ratio of 3:1, as observed. J varied from 77 G in $CHCl_3$ to 92 G in CS_2, with no obvious correlation with commonly cited solvent characteristics.

Reduction of the nitroxyl by addition of phenylhydrazine[8] converts the spectrum of V to that of VII.

Preliminary results for related complexes indicate that the metal-nitroxyl interaction is very sensitive to the details of as yet unidentified molecular parameters. For example, replacement of the amide linkage in III by an ester linkage (VIII) yields a spectrum which does not have any features identifiable as "nitroxyl". Reduction of VIII with phenylhydrazine also returns the spectrum to that of the nonnitroxyl analogue.

Owing to the clearly defined splitting of the nitroxyl region of the spectrum in V, the magnitude of the exchange interaction can be obtained directly. The extent to which dipolar interactions affect the EPR spectrum cannot be proven without further studies, which are in progress. The relative contributions of exchange and dipolar effects may be dependent on electron spin relaxation time and molecular tumbling correlation times as well as details of metal-nitroxyl distance and nature of the intervening bonds.[9] Thus the observation of exchange in these spin-labeled copper porphyrin complexes does not prove that exchange contributes to the line shape of the nitroxyl in spin-labeled hemoproteins. Nevertheless, interpretation should proceed cautiously, considering quantitative data on both the metal and the nitroxyl EPR spectra.

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References and Notes

(1) H. M. McConnell and J. C. A. Boeyens, *J. Phys. Chem.*, **71**, 12 (1967).
(2) (a) T. Asakura, J. S. Leigh, Jr., H. R. Drott, T. Yonetani, and B. Chance, *Proc. Natl. Acad. Sci. U.S.A.*, **68**, 861 (1971); (b) T. Asakura and M. Tamura, *J. Biol. Chem.*, **249**, 4504 (1974), and references therein.
(3) (a) J. S. Taylor, J. S. Leigh, Jr., and M. Cohn, *Proc. Natl. Acad. Sci. U.S.A.*, **64**, 219 (1969); (b) J. S. Leigh, Jr., *J. Chem. Phys.*, **52**, 2608 (1970).
(4) F. P. Schwarz, M. Gouterman, Z. Muljiani, and D. H. Dolphin, *Bioinorg. Chem.*, **2**, 1 (1972).
(5) (a) P. T. Manoharan and M. R. Rogers in "Electron Spin Resonance of Metal Complexes", T. F. Yen, Ed., Plenum Press, New York, N.Y., 1969, p 143; (b) J. Subramanian in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, p 555.
(6) I. C. P. Smith in "Biological Applications of Electron Spin Resonance", H. M. Swartz et al., Ed., Wiley, New York, N.Y., 1972, p 483.
(7) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy", Vol. 1, Pergamon Press, Elmsford, N.Y., 1965, p 310.
(8) T. D. Lee and J. F. W. Keana, *J. Org. Chem.*, **40**, 3145 (1975).
(9) The studies of exchange in diradicals and dipolar and exchange terms in metal-nitroxyl collisions caution that subtle and complicated effects may be observed: (a) E. K. Metzner, L. J. Libertini, and M. Calvin, *J. Am. Chem. Soc.*, **96**, 6515 (1974); (b) K. M. Salikhov, A. B. Doctorov, Yu. N. Molin, and K. I. Zamaraev, *J. Mag. Res.*, **5**, 189 (1971), and references therein.
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Photochemical Reaction Pathways of Ruthenium(III) Complexes. Ultraviolet Irradiation of Tris(*N,N*-dialkyldithiocarbamato)ruthenium(III)

Sir:

The photochemical behavior of metal complexes with sulfur-coordinating ligands has received little attention.[1-4] The electronic absorption spectra of complexes with the MS_6 core are very rich, consisting primarily of intense charge-transfer bands which extend well into the visible region of the spectrum.[5,6] Therefore, the photochemistry of these complexes is expected to be characteristic of reactions from charge transfer excited states. For example, electron transfer from ligand to metal (CTTM) resulting in oxidized ligand dissociation and metal reduction is commonly found.[7] The reactivity of charge-transfer excited states is currently receiving considerable attention due in part to recent interest in photocatalysis[8] and solar energy conversion[9] and because few systematic studies have been done on complexes other than the cobalt(III) amines.[7] We are in the process of studying the charge-transfer photochemistry of metal complexes with sulfur-containing ligands[4] and report here the results of experiments which demonstrate the rich photochemistry of tris(*N,N*-dialkyldithiocarbamato)ruthenium(III), $Ru(R_2dtc)_3$, complexes.

Irradiation at $\lambda = 265$ nm[10] of $Ru(R_2dtc)_3$[11] where R = methyl or ethyl in $CHCl_3$, CH_2Cl_2, or C_6H_5Cl solution at 30 °C yields only two ruthenium-containing products, **1a** and **1b**, according to eq **1**.

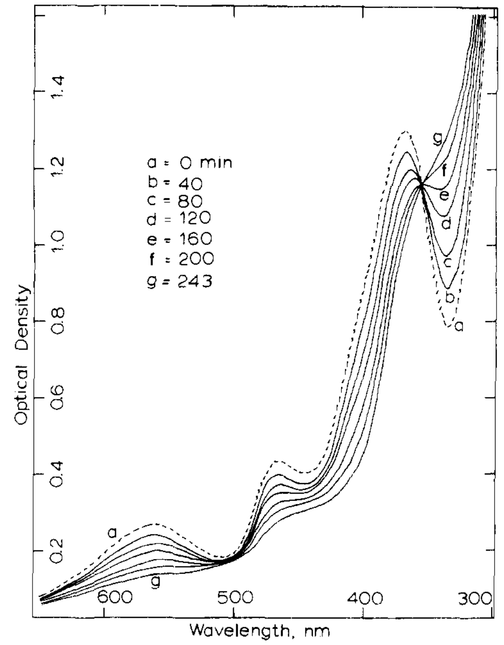
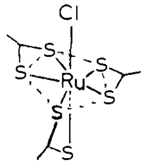


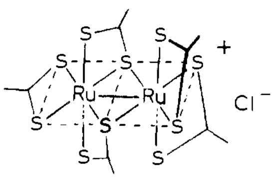
Figure 1. Spectral changes during photolysis at 265 nm of $Ru(Et_2dtc)_3$ in $CHCl_3$ solution. Line a is due to $Ru(Et_2dtc)_3$. Line g results after ~80% of $Ru(Et_2dtc)_3$ is converted into an 80:20 mol ratio of $ClRu(Et_2dtc)_3$ and α-$[Ru_2(Et_2dtc)_5]Cl$, respectively (see text).

$$Ru(R_2dtc)_3 \xrightarrow{h\nu} \underset{\mathbf{1a}}{ClRu(R_2dtc)_3} + \underset{\mathbf{1b}}{\alpha\text{-}[Ru_2(R_2dtc)_5]Cl} \quad (1)$$

The identification[12] of compounds **1a** and **1b** was made by comparison of their ^1H NMR and electronic absorption spectra with spectra from authentic samples.[13,14] The structures of **1a**[13] and **1b**[14] have recently been determined. The spectral changes during photolysis of $Ru(Et_2dtc)_3$ in $CHCl_3$ solution at $\lambda = 265$ nm and 30 °C are shown in Figure 1. The appearance of an isosbestic point at $\lambda = 356$ nm results only if **1a** and **1b** are formed in the mole ratio (**1a**:**1b**) of 79:21.[15] Similar photolysis experiments with $Ru(Me_2dtc)_3$ using $CHCl_3$ and CH_2Cl_2 at 0 °C were monitored by ^1H NMR spectroscopy. The growth of signals due to **1a** and **1b** is clearly evident and is shown in Figure 2 for irradiation in $CHCl_3$ solvent. The results are essentially identical for $CHCl_3$ and CH_2Cl_2 solvents and signal integration using peak heights yields a mole ratio (**1a**:**1b**) of 82:18 which is constant with time.[16] These results indicate that the same reaction mechanism is operative for R = methyl and ethyl and for $CHCl_3$ and CH_2Cl_2 solvents.



1a



1b

Quantum yields were measured at 30 °C for irradiation at $\lambda = 265$, 313, and 366 nm by monitoring spectral changes at 560, 470, and 370 nm, where $Ru(Et_2dtc)_3$ has absorption maxima.[17] The quantum yields for disappearance of $Ru(Et_2dtc)_3$ in $CHCl_3$ solution at 30 °C are $\Phi = 0.29$, 0.071, and 0.010 at 265, 313, and 366 nm, respectively. These values were constant in the range of 0–20% conversion of $Ru(Et_2dtc)_3$ to products. The quantum yields indicate that the photoactive band or bands in $Ru(Et_2dtc)_3$ are in the 265-nm region where several intense charge-transfer absorptions exist. These bands and their extinction coefficients in $CHCl_3$ are λ_{max} 284 nm (ϵ 28 200 M^{-1} cm^{-1} and 260 (38 900). St. Nikolov[6] has assigned bands in this region as CTTM $\pi \rightarrow e^*$. It is likely that the smaller quantum yields found at 313 and 366 nm result from irradiation of the weakly absorbing shoulder of the intense CT bands at 260 and 284 nm, rather than from irradiation of the 370-nm band. This is consistent with Φ being smaller at 366 than at 313 nm, since the 370-nm band is more intense at 366 nm whereas the CT shoulders are more intense at 313 nm. Therefore, the excited state should have increased electron density in antibonding metal orbitals which will promote ligand oxidation and ruthenium reduction. A similar excited state has been proposed to account for the photochemistry of $Fe(R_2dtc)_3$ where R = ethyl or benzyl.[3,4] Irradiation of $Fe(Et_2dtc)_3$ at 265 nm in dilute C_6H_5Cl (benzene or acetonitrile solvent) yields $ClFe(Et_2dtc)_2$ and $C_6H_5SC(S)N(C_2H_5)_2$ quantitatively, with the quantum yield for $Fe(Et_2dtc)_3$ disappearance in neat C_6H_5Cl, Φ_{265}, equal to 0.39.[4,18]

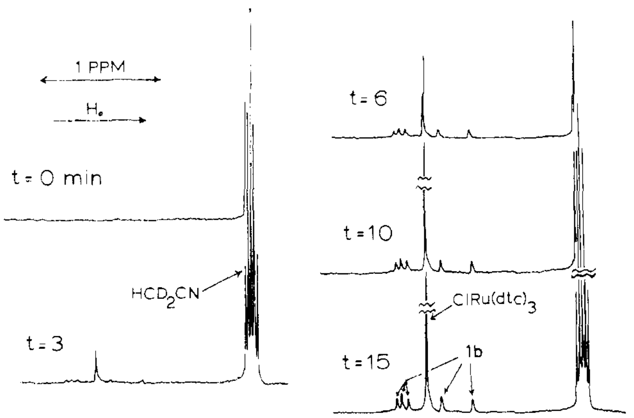
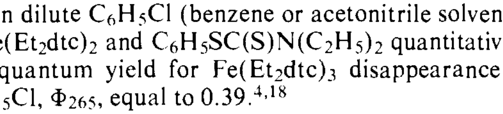


Figure 2. ^1H NMR of the reaction mixture at various times during photolysis at 265 nm of $Ru(Me_2dtc)_3$ in $CHCl_3$ at 0 °C. Spectra were recorded in CD_3CN solvent at 100 MHz. The reaction is ~85% complete for the t = 15 min trace.

Photolysis of $Ru(Et_2dtc)_3$ was also carried out using dilute C_6H_5Cl solutions in benzene and acetonitrile. In these experiments the concentrations of complex ($\sim 1 \times 10^{-3}$ M) and C_6H_5Cl (~0.01 M) were selected to eliminate C_6H_5Cl photolysis. An isosbestic point at ~356 nm was observed in both cases, which indicates that the ruthenium containing products, **1a** and **1b**, are formed in the same relative yield as with photolysis in $CHCl_3$ and CH_2Cl_2. The nonvolatile organic products of the reaction were isolated by extraction of the solid residue with pentane followed by GLC-MS analysis. A small amount of $C_6H_5SC(S)N(C_2H_5)_2$ was found which accounts for ~20% of the $S_2CN(C_2H_5)_2$ lost in formation of the observed amount of α-$[Ru_2(Et_2dtc)_5]Cl$.[19] Since $C_6H_5SC(S)N(C_2H_5)_2$ is known to undergo secondary photolysis,[4] this yield is not inconsistent with the ester being the primary $S_2CN(C_2H_5)_2$-containing organic product.

A proposed mechanism for reaction 1 is shown in steps 2a–d. The excited state in step 2a most likely results from a CTTM transition and therefore possesses reduced metal and oxidized ligand character. This excited state reacts with RCl via two



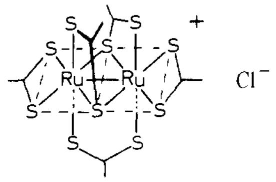
(2a)

$$[Ru(R_2dtc)_3]^* + R'Cl \longrightarrow \underset{\mathbf{1a}}{ClRu(R_2dtc)_3} + R'\cdot \quad (2b)$$

$$[Ru(R_2dtc)_3]^* + R'Cl \longrightarrow \text{"}ClRu(R_2dtc)_2\text{"} + R'dtc \quad (2c)$$

$$\text{"}ClRu(dtc)_2\text{"} + Ru(dtc)_3 \longrightarrow \underset{\mathbf{1b}}{\alpha\text{-}[Ru_2(dtc)_5]^+Cl} \quad (2d)$$

pathways. Pathway 2b involves chlorine abstraction resulting in the ruthenium(IV) complex, 1a, and an organic free radical, R′·, which subsequently reacts with solvent. Pathway 2c is proposed because it is the primary reaction of the iron analogue[3,4,18] and it accounts for the presence of the ester, R′dtc, where R′ = phenyl. The complex $ClRu(R_2dtc)_2$ has never been isolated nor has it been synthesized by other means.[13] The formation of **1b** results from reaction of $ClRu(R_2dtc)_2$ with $Ru(R_2dtc)_3$ and subsequent electron transfer to chlorine, yielding $\alpha[Ru_2(R_2dtc)_5]^+Cl^-$. Complex **1b** converts into β-$[Ru_2(R_2dtc)_5]^+ Cl^-$ (**2**) thermally in solution.[14,20]



2

The excited state of $Ru(R_2dtc)_3$ shown in 2a is considered likely because chemically reduced air-sensitive R_2dtc complexes of Fe(II) or bimetallic Ru(II)-Ru(III) are known to abstract chlorine radicals from $CHCl_3$ or CH_2Cl_2 in the dark.[4,18,21] Excited states which contain oxidized ruthenium would not be expected to show chlorine abstraction. It is possible that $[Ru(R_2dtc)_3]^*$ contains an intraligand excited state or that reaction 2a results from CT transitions which directly involve solvent. Neither of these possibilities can be eliminated; however, the UV-vis absorption spectrum of $Ru(Et_2dtc)_3$ is virtually identical in $CHCl_3$, CH_3CN, and C_6H_6 solvents, which suggests little or no specific solvent interaction. Since the rate of step 2d in the mechanism is likely to be concentration dependent,[22] experiments were carried out for initial concentrations of $Ru(R_2dtc)_3$ in $CHCl_3$ between 1.0×10^{-4} and 7.5×10^{-4} M. The disappearance quantum yield for 265-nm irradiation was constant ($\Phi = 0.29 \pm 0.01$) over this range. In addition, the product distribution was found to be independent of initial $Ru(R_2dtc)_3$ concentration between $\sim 1 \times 10^{-4}$ and 5×10^{-3} M, within experimental error of ^1H NMR integration. These experiments suggest that the product distribution is dictated by the relative rates of steps 2b and 2c and, since 2b is the major route, the expected concentration dependence of Φ may not be detectable over the experimentally accessible concentration range. Electrochemical and redox experiments are in progress which should test the proposed mechanism.

The diruthenium complexes **1b** and **2** do not react photochemically under the above conditions; however, prolonged irradiation of either compound in CH_3CN solution slowly yields a mixture of **1b** and **2**. An alternate pathway for the formation of **1b** could involve photolysis of **1a** in the presence of $Ru(dtc)_3$. This reaction has been studied in CH_3CN solvent and does occur, however, with a quantum yield for disappearance of $Ru(dtc)_3$, Φ_{265}, equal to only 0.015.[23] This reaction is too slow to account for the 20 mol % of **1b** observed. Also, as shown in Figure 2, **1a** and **1b** are formed simultaneously and their mole ratio is constant for at least 40-95% reaction.

We have very carefully tried to eliminate solvent photolysis in the above experiments. Irradiation in $CHCl_3$ and CH_2Cl_2 solution at $\lambda \geq 265$ nm should effectively prevent solvent photolysis since the absorbances of these solvents are <0.026 and 0.006 at 265 nm, respectively, for a 1-cm pathlength. In addition, for typical experimental concentrations the metal complexes are strongly absorbing ($A \gg 2$) in the region where the solvents have absorbance. Experiments using C_6H_5Cl do involve some solvent photolysis; however, internal filtering via strong complex absorption and the use of dilute C_6H_5Cl solutions should minimize this. Finally, the product distribution is invariant in these three solvents, suggesting that the same mechanism is operative.

A photolysis experiment was carried out on $Ru(Et_2dtc)_3$ in $CHCl_3$ solution where the solvent was intentionally irradiated (predominant irradiating wavelengths of 238, 240, and 248 nm). In this case essentially the same product distribution was observed (isosbestic point at 358 nm) and the quantum yield Φ was 0.5. This result suggests that chlorine radical formation via $CHCl_3$ irradiation leads to the same reaction as that which is initiated by complex absorption and subsequent energy transfer to solvent, which must occur in steps 2b and 2c since C-Cl bond cleavage results. Additional experiments are currently being carried out which should elucidate the role of the solvent in these reactions.

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References and Notes

(1) J. P. Fackler, Jr., A. Avdeef, and R. G. Fischer, Jr., *J. Am. Chem. Soc.*, **95**, 774 (1973).

(2) D. P. Schwendiman and J. I. Zink, *J. Am. Chem. Soc.*, **98**, 1248 (1976).

(3) D. P. Schwendiman and J. I. Zink, *J. Am. Chem. Soc.*, **98**, 4439 (1976).

(4) G. L. Miessler, G. Stuk, T. P. Smith, K. W. Given, M. C. Palazzotto, and L. H. Pignolet, *Inorg. Chem.*, **15**, 1982 (1976).

(5) C. K. Jorgensen, *J. Inorg. Nucl. Chem.*, **24**, 1952; *Progr. Inorg. Chem.*, **12**, 101 (1970).

(6) G. St. Nikolov, *Inorg. Chim. Acta*, **4**, 610 (1970).

(7) J. F. Endicott in "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Wiley-Interscience, New York, N.Y., 1975, Chapter 3 and references cited therein.

(8) M. Wrighton, *Chem. Rev.*, **74**, 401 (1974).

(9) See, for example, V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and M. Gleria, *Science*, **189**, 852 (1975); G. Spritschnik, H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, *J. Am. Chem. Soc.*, **98**, 2337 (1976).

(10) All photolysis experiments were carried out in quartz vessels at 30 or 0 °C under a purified N_2 atmosphere using filtered or unfiltered radiation from mercury vapor lamps. The 265-nm band was isolated with an Optics Technology interference filter number 270. Either a low-intensity Hg-vapor lamp (U-shaped low-pressure Hg lamp from Hanovia, type SH) or an Ace 2130 immersion lamp (low-pressure Hg lamp) was employed for all experiments. The chlorinated solvents used in photolysis experiments were freshly distilled from BaO, stored under a N_2 atmosphere, and passed through an alumina column just prior to use.

(11) For the synthesis and strucutre of $Ru(Et_2dtc)_3$, see L. H. Pignolet, *Inorg. Chem.*, **13**, 2051 (1974).

(12) Compounds **1a** and **1b** are easily separated by column chromatography on silica gel or alumina. Compound **1a** is eluted off the column using acetone while **1b** requires methanol. The ^1H NMR spectra of the pure compounds (R = CH_3 and C_2H_5) were recorded in CD_3CN and CD_2Cl_2 solvents.

(13) K. W. Given, B. M. Mattson, and L. H. Pignolet, *Inorg. Chem.*, **15**, 3152 (1976).

(14) A. R. Hendrickson, J. M. Hope, and R. M. Martin, *J. Chem. Soc., Dalton, Trans.* 2032 (1976).

(15) Careful product analysis shows that **1a** and **1b** are the only species formed which absorb at 356 nm; therefore a knowledge of the molar extinction coefficients for **1a**, **1b**, and $Ru(Et_2dtc)_3$ in $CHCl_3$ at 30 °C (ϵ 9200, 1100, and 8460 M^{-1} cm^{-1}, respectively) allows the molar ratio of **1a** and **1b** to be calculated. The ratio is accurate to within ±3%.

(16) Aliquot samples were removed from the reaction mixture at various time intervals, evaporated to dryness, and dissolved in CD_3CN for ^1H NMR analysis. The maximum and minimum mole ratios calculated between 40 and 95% completeness of reaction are 85:15 and 79:21, respectively.

(17) Quantum yields were determined as described in ref 4 using ferrioxalate actinometry.

(18) G. L. Miessler, M. F. McGuiggan, and L. H. Pignolet, unpublished work.

(19) It is assumed that one Et_2dtc ligand radical is lost for each molecule of **1b** formed.

(20) B. M. Mattson, J. R. Heiman, and L. H. Pignolet, *Inorg. Chem.*, **15**, 564 (1976).

(21) S. H. Wheeler, B. M. Mattson, K. W. Given, and L. H. Pignolet, unpublished work.

(22) The scavenging steps **2b** and **2c** are expected to be diffusion controlled as was recently found with the similar iron reaction: Po-Hsin Liu and J. I. Zink, *J. Am. Chem. Soc.*, **99**, 2155 (1977).

(23) This reaction was carried out with an equimolar mixture of $ClRu(Et_2dtc)_3$ and $Ru(Et_2dtc)_3$ at 30 °C.

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