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Catalytic Displacement of CO by Phosphine Ligands from $Ru_3(CO)_{12}$ Promoted by Salts of Various Hydrido Anions: $[PPN][HRu_3(CO)_{11}]$, $[PPN][HRu(CO)_4]$, and K-Selectride

Sir:

In attempts to extend the scope of reaction 1[1] to include the PPN^+ salts (PPN^+ = bis(triphenylphosphine)nitrogen(1+)) of a variety of nucleophilic anions, we observed that a number of hydrido anions also promote the monosubstitution of CO by PPh_3 in $Ru_3(CO)_{12}$ over a broad range of rates depending on the hydride-donating properties of these salts:

$$Ru_3(CO)_{12} + PR_3 \xrightarrow[\text{THF soln, 25 °C}]{\text{catalyst}} Ru_3(CO)_{11}PR_3 + CO \qquad (1)$$

Catalyst precursors for this reaction are as follows: (a) $[PPN][Nu]$; Nu^- = CN^-, CH_3COO^-, F^-, Cl^-, Br^-, I^-;[1] (b) hydride donors (this work) (i) $[PPN][HRu_3(CO)_{11}]$, (ii) $[PPN][HRu_3(CO)_{10}PPh_3]$, (iii) $[PPN][HRu_3(CO)_{10}PPh_3]$, CO atmosphere, (iv) $[PPN][HRu(CO)_4]$, and (v) K-Selectride (Aldrich).

Following the preliminary observation of a moderate efficiency of $[PPN][BH_4]$ as a catalyst precursor for reaction 1, we checked the intermediacy of $[HRu_3(CO)_{11}]^-$ in the catalytic cycle. Indeed, in the absence of phosphine ligand, this anion is rapidly and quantitatively obtained from the stoichiometric reaction of $[PPN][BH_4]$[2] with $Ru_3(CO)_{12}$.[3] Thus, we attempted to initiate reaction 1 by using catalytic amounts of $[PPN][HRu_3(CO)_{11}]$.[4]

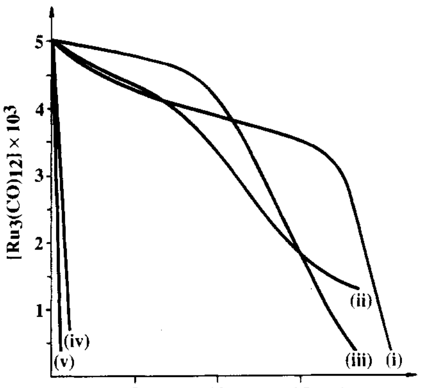

Figure 1. In situ infrared monitoring of reaction 1, with the concentration of $Ru_3(CO)_{12}$ plotted as a function of time for various catalyst precursors: (i) $[PPN][HRu_3(CO)_{11}]$, 10^{-3} M, turnover frequency (measured in the linear part of the plot) ~1 min^{-1}; (ii) $[PPN][HRu_3(CO)_{10}PPh_3]$, 5×10^{-4} M; (iii) $[PPN][HRu_3(CO)_{10}PPh_3]$ (under a CO atmosphere), 5×10^{-4} M, turnover ~1 min^{-1}; (iv) $[PPN][HRu(CO)_4]$, 5×10^{-4} M, turnover ~8.3 min^{-1}; (v) K-Selectride, 5×10^{-4} M, turnover ~20 min^{-1}. Experimental conditions:[4] tetrahydrofuran, 30 mL; $Ru_3(CO)_{12}$, 5×10^{-3} M; PPh_3, 2×10^{-2} M; temperature, 25 °C.

In situ infrared monitoring (Figure 1) showed an induction period of ca. 16 min followed by a net acceleration leading to completion of the substitution reaction within ca. 3 min more, with a zero-order dependence on the concentration of $Ru_3(CO)_{12}$; the monosubstituted derivative $Ru_3(CO)_{11}PPh_3$ was obtained as the principal reaction product. Traces of the disubstituted complex $Ru_3(CO)_{10}(PPh_3)_2$, formed from the facile (noncatalyzed) reaction of $Ru_3(CO)_{11}(PPh_3)$ with excess triphenylphosphine,[1,5] were also observed.

According to Ford and co-workers,[6] $[HRu_3(CO)_{11}]^-$ exhibits an enhanced substitutional lability relative to that of $Ru_3(CO)_{12}$ resulting in rapid formation of $[HRu_3(CO)_{10}(PR_3)]^-$ (reaction 2).

$$[HRu_3(CO)_{11}]^- + PR_3 \rightarrow [HRu_3(CO)_{10}(PR_3)]^- + CO \qquad (2)$$

In order to evaluate the intermediacy of $[HRu_3(CO)_{10}(PR_3)]^-$ in reaction 1, this complex was prepared separately and subsequently used to activate the system. Catalytic reaction was found to take place with a shorter induction period than with $[HRu_3(CO)_{11}]^-$, even when starting from smaller amounts of catalyst (Figure 1).[4] A decrease of activity was observed during the reaction and attributed to a lack of carbon monoxide to regenerate the undecacarbonyl species. Conversely, when the same reaction

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[1] Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647.

[2] $[PPN][BH_4]$ is prepared according to a published procedure: Kirtley, S. W.; Andrews, M. A.; Bau, R.; Grynkewich, G. W.; Marks, T. J.; Tipton, D. L.; Whittlesey, B. R. *J. Am. Chem. Soc.* **1977**, *99*, 7154.

[3] (a) We find that direct addition of $[PPN][BH_4]$ (433 mg, 0.782 mmol, dissolved in ca. 3 mL of dichloromethane) to a THF solution (100 mL) of $Ru_3(CO)_{12}$ (500 mg, 0.782 mmol) at ambient temperature gives $[PPN][HRu_3(CO)_{11}]$ in quantitative spectroscopic yield within less than 3 min. After the THF solution is evaporated, subsequent recrystallization of the complex is made from a dichloromethane–ethanol mixture at −30 °C (yield 80%). This simple and direct procedure is faster than the classic route from $NaBH_4$[3b] or the alternate synthesis[3c] involving $[NEt_4][BH_4]$ in dichloromethane solution (the latter reaction was found to take 1 h in this solvent). (b) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Süss, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1356. (c) Gibson, D. H.; Ahmed, F. U.; Phillips, K. R. *J. Organomet. Chem.* **1981**, *218*, 325.

[4] A tetrahydrofuran solution (30 mL) of $Ru_3(CO)_{12}$ (96 mg, 0.15 mmol; concentration 5×10^{-3} M) and excess PPh_3 (157 mg, 0.6 mmol; concentration 2×10^{-2} M) was stirred at 25 °C in a Schlenk flask under nitrogen. Crystals of $[PPN][HRu_3(CO)_{11}]$ (34 mg; one-fifth of the stoichiometric amount) were then added. The solution was circulated through a 0.1-mm CaF_2 cell with a lab pump (Fluid Metering, Inc.; Model RP-D), for in situ monitoring. The spectrophotometer (Perkin-Elmer 337) was locked on the 2060-cm^{-1} absorption band of $Ru_3(CO)_{12}$. The plots were scaled from standard solutions of $Ru_3(CO)_{12}$ at various concentrations. In subsequent experiments, the following catalyst precursors were added in smaller amounts (one-tenth of the stoichiometric amount) due to their higher efficiency: crystals of $[PPN][HRu_3(CO)_{10}(PPh_3)]$ (prepared according to the published procedure[6]) (20.8 mg); crystals of $[PPN][HRu(CO)_4]$ (11 mg); K-Selectride (potassium tri-*sec*-butylborohydride) 0.015 mmol (added in THF solution).

[5] Malik, S. K.; Poë, A. J. *Inorg. Chem.* **1978**, *17*, 1484.

[6] Taube, D. J.; Ford, P. C. *Organometallics* **1986**, *5*, 99.

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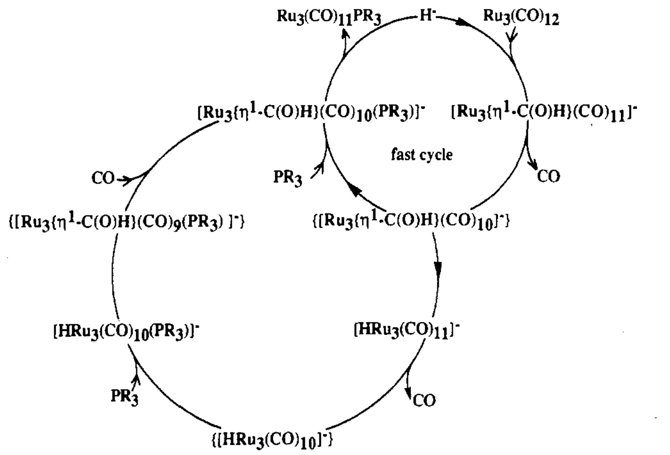

Figure 2. Proposed mechanism for the catalytic substitution of CO by phosphines in $Ru_3(CO)_{12}$ promoted by hydrido anions. Intermediate unsaturated species are shown in brackets.

was conducted under a CO atmosphere, the second part of the plot showed a zero-order linear decrease, without any loss of activity (Figure 1).[4]

The catalysis can be interpreted in terms of the hydride-donating properties of $[HRu_3(CO)_{10}(PR_3)]^-$ in the presence of CO (reaction 3).

$$[HRu_3(CO)_{10}(PR_3)]^- + CO \rightarrow Ru_3(CO)_{11}(PR_3) + H^- \qquad (3)$$

Hydride transfer from $[HRu_3(CO)_{11}]^-$ to $[B(OMe)_3]$, or to H_2O, has been observed by Shore and co-workers.[7] Due to the higher electron density of the substituted derivative $[HRu_3(CO)_{10}(PR_3)]^-$, such hydride-donating properties are markedly enhanced for the latter species, as evidenced by the observation that related substituted derivatives $[HRu_3(CO)_9(dppe)]^-$ and $[HRu_3(CO)_7(dppm)_2]^-$ react 5–7 times faster with H_2O than $[HRu_3(CO)_{11}]^-$;[7a] furthermore, intermolecular hydride transfer from $[HRu_3(CO)_9(dppe)]^-$ to a carbonyl group of a mononuclear ruthenium complex has been observed.[8]

Accordingly, the equilibrium (3) is displaced to the right in the presence of a substrate with hydride-acceptor ability. Hence, nucleophilic attack of hydride at $Ru_3(CO)_{12}$ (likely at the carbon of a coordinated CO) is part of the catalytic cycle

$$Ru_3(CO)_{12} + H^- \rightarrow [Ru_3\{\eta^1\text{-}C(O)H\}(CO)_{11}]^- \qquad (4)$$

Though the formyl complex $[M_3\{\eta^1\text{-}C(O)H\}(CO)_{11}]^-$ (M = Ru, Os) has a lifetime of several hours in the case of osmium,[9] it is much more unstable for ruthenium,[10] where it undergoes rapid CO elimination in the absence of coordinative ligands to give $[HRu_3(CO)_{11}]^-$.

The existence of an induction period when reaction 1 is initiated by $[HRu_3(CO)_{11}]^-$ or $[HRu_3(CO)_{10}(PR_3)]^-$ clearly indicates that these complexes are not part of the rapid catalytic cycle but are efficient precursors to the active species. This suggests that in all catalytic substitution reactions promoted by nucleophilic anions, a reactive intermediate must be trapped by the phosphine ligand at an early stage of nucleophilic attack.[11] In the present case, the active intermediate may be the adduct roughly formulated as "$[HRu_3(CO)_{12}]^-$", containing a hydridic terminal hydrogen bound either to a carbon atom of a formyl group[9,10] or to a metal in an "open" structure.[12] Both possibilities have been considered to account for the hydride-donating properties of $[HRu_3(CO)_{11}]^-$[7] or other hydrido anions.[13] A reasonable catalytic cycle based on the formyl intermediate is shown in Figure 2.[14] Competitive trapping of the active species by carbon monoxide and phosphine ligands prevents its temporary loss into the slow catalytic cycle involving $[HRu_3(CO)_{11}]^-$. Whenever this happens, the presence of carbon monoxide in solution favors further regeneration of the active species; it also improves the selectivity in the monosubstituted complex.

In light of these observations, any efficient hydride donor should provide direct entry into the fast catalytic cycle. This is observed when $[PPN][HRu(CO)_4]$ and K-Selectride are used as sources of H^- (Figure 1, reaction 1, catalysts iv and v, respectively). In both these cases, a fast reaction takes place without an induction period. Typically, for a catalyst concentration of 5×10^{-4} M in K-Selectride, the turnover frequency is ca. 20 min^{-1} under our experimental conditions.[4,15]

While all these observations are fully consistent with a hydride transfer, the possibility of electron transfer cannot be totally excluded, though it seems very unlikely. Indeed, there are two arguments against electron transfer in the present case. First, the radical anion $[Ru_3(CO)_{12}]^{\bullet-}$ has a very short lifetime, on the order of 10^{-6} s,[16,17] which renders it very unlikely to participate in a simple ETC mechanism. Second, it has been previously shown that the radical anion $[HRu_3(CO)_{11}]^{\bullet-}$ (prepared at −78 °C)[7a] is extremely unstable, since no ESR signal can be detected above −20 °C. Besides, we note that recent studies of photosubstitutions of $Ru_3(CO)_{12}$ also provide evidence for a nonradical mechanism.[18]

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(7) (a) Bricker, J. C.; Nagel, C. C.; Shore, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 1444. (b) *Ibid.* **1985**, *107*, 377. (c) When this work was reviewed, we became aware that Shore and co-workers have recently succeeded in separating KH and $Ru_3(CO)_{12}$ from the reaction of $K[HRu_3(CO)_{11}]$ with CO (unpublished observations).

(8) Barratt, D. S.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1559.

(9) (a) Steinmetz, G. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 1278. (b) Steinmetz, G. R.; Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 2559.

(10) Schoening, R. C.; Vidal, J. L.; Fiato, R. A. *J. Organomet. Chem.* **1981**, *206*, C43.

(11) During earlier studies in collaboration with Kaesz, H. D. we noticed[1] erratic results in the case of substitutions promoted by Cl^-. These results are due to the formation of $[PPN][Ru_3(CO)_{10}(\mu\text{-}Cl)]$. Such a deactivated system can be reactivated by two procedures: (a) Bubbling CO into the solution regenerates $[PPN][Ru_3(CO)_{11}Cl]$, where the nucleophile occupies a terminal position, and reactivates the catalysis. (b) Interestingly, we also noticed (footnote 13 in ref 1) an effect of traces of water on the system involving Cl^-. We can now understand this on the basis of the above results: reaction of a nucleophile with water may liberate OH^-, which subsequently generates $[HRu_3(CO)_{11}]^-$ and provides entry into a catalytic system that then involves hydride transfer; in that case, the nature of the active nucleophile has been changed.

(12) Payne, M. W.; Leussing, D. L.; Shore, S. G. *J. Am. Chem. Soc.* **1987**, *109*, 617.

(13) The system may have some relevance to the Chatt synthesis of substituted group VIB (6^{20}) metal carbonyls catalyzed by borohydride anions: Chatt, J.; Leigh, G. J.; Thankarajan, N. *J. Organomet. Chem.* **1971**, *29*, 105. Interestingly, this reaction was subsequently shown to involve a binuclear hydrido-bridged metal–metal-bonded anionic species at an intermediate step: Darensbourg, M. Y.; Walker, N.; Burch, R. R., Jr. *Inorg. Chem.* **1978**, *17*, 52.

(14) (a) Several steps within this cycle are analogous with those suggested by Ford and co-workers in the case of the stoichiometric displacement of CO by trimethyl phosphite from $Ru_3(CO)_{12}$ promoted by OCH_3^-: Anstock, M.; Taube, D.; Gross, D. C.; Ford, P. C. *J. Am. Chem. Soc.* **1984**, *106*, 3696. (b) A closely related cycle may be constructed on the alternate hypothesis that the active hydride-transfer agent has an open structure where the hydride is terminally bound to the metal.[12] However, there is no spectroscopic evidence for such a complex, while the formyl complex is at least detectable at low temperature.[10]

(15) (a) K-Selectride is a better hydride donor than $[PPN][BH_4]$; the rates observed with $[PPN][BH_4]$ are of the same magnitude as those observed with $[HRu_3(CO)_{11}]^-$. The rates observed with superhydrides are matching those reported for the PPN^+ salts of the highly active anions CN^-, CH_3COO^-, or F^-.[1] However, a precise comparison of our values with those already published for these anions is not possible since the former values were obtained from solid samples of these poorly soluble salts. The recent isolation of a variety of anion-promoted metal clusters, $[PPN][Ru_3(CO)_{11}(Nu)]$ (Nu = CN^-;[15b] Nu = Cl^-, Br^-, I^-, CH_3COO^-;[15c] all highly soluble in THF) will allow a direct and precise comparison of the rates (Lavigne, G., current studies in collaboration with H. D. Kaesz). (b) Lavigne, G.; Lugan, N.; Bonnet, J.-J. *J. Chem. Soc., Chem. Commun.*, in press. (c) Lavigne, G., unpublished results.

(16) Cyr, J. C.; DeGray, J. A.; Gosser, D. K.; Lee, E. S.; Rieger, P. H. *Organometallics* **1985**, *4*, 950 and references therein.

(17) Downward, A. J.; Robinson, B. H.; Simpson, J.; Bond, A. M. *J. Organomet. Chem.* **1987**, *320*, 363.

We are currently attempting to apply spin-trap techniques to check for the eventual formation of radical anions.[19] However, it is difficult to find a radical trap that is unreactive toward hydride donors.

Finally, we wish to underscore the synthetic utility of the reported reaction, given that many "superhydrides" are available in a laboratory. By extension, any good hydride donor will function as an apparent catalyst precursor for substitution reactions of $Ru_3(CO)_{12}$.

Acknowledgment. Special thanks are extended to Herbert D. Kaesz for helpful discussions regarding this work. Financial support from the CNRS is gratefully acknowledged. We are also grateful to Johnson-Matthey for generous loans of ruthenium trichloride.

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(18) Desrosiers, M. R.; Wink, D. A.; Trautman, R.; Friedman, A. E.; Ford, C. *J. Am. Chem. Soc.* **1986**, *108*, 1917.

(19) Smith, G.; Sutcliffe, L. H.; Cole Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1984**, 1209.

(20) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Pressure Tuning of Exchange Interactions in Dinuclear Chromium(III) Complexes

Sir:

Luminescence spectroscopy has proved to be a very powerful tool for probing exchange interactions in dinuclear chromium(III) complexes. This communication reports the first experiments under high pressure. They allow a study of the pressure and volume dependence of the exchange. The investigated complexes are $[LCr^{III}(OH)_3Cr^{III}L](ClO_4)_3$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane; the complex is abbreviated $\{triol\}(ClO_4)_3$ in the following) and $[(NH_3)_5Cr^{III}OHCr^{III}(NH_3)_5]Cl_5{\cdot}H_2O$ (abbreviated $\{rhodo\}Cl_5{\cdot}H_2O$). Dramatic shifts of the luminescence line positions up to several hundred wavenumbers are observed upon application of a hydrostatic pressure of 40 kbar. The effects are 1 order of magnitude larger than for the ruby R lines.[1] A detailed account of this work is given in ref 1, and the pressure cell is described in ref 2.

Figure 1 shows 14 K luminescence spectra of $\{triol\}(ClO_4)_3$ at three pressures obtained by using a 4:1 methanol/ethanol mixture as a pressure-transmitting medium.[2] The emitting dimer state in this complex is a spin triplet, and the dominant peak in the emission spectrum corresponds to the spin-allowed $S^* = 1 \rightarrow S = 1$ transition.[3,4] The energy shifts are accompanied by a broadening of the lines that is due to nonhydrostatic pressure components. In Figure 2 the observed energy differences between the dimer ground-state levels in $\{triol\}(ClO_4)_3$ are plotted as a function of the applied pressure. The dependence is linear within the pressure range examined here: $\delta(E(S = 1) - E(S = 0)) = 1.3 \pm 0.1\ cm^{-1}\ kbar^{-1}\ P^{-1}$ and $\delta(E(S = 2) - E(S = 0)) = 2.6 \pm 0.15\ cm^{-1}\ kbar^{-1}\ P^{-1}$. The energy differences over the whole pressure range are well accounted for by the eigenvalues of the Hamiltonian

$$H_{ex} = -2J\vec{S}_1\cdot\vec{S}_2 - j(\vec{S}_1\cdot\vec{S}_2)^2 \qquad (1)$$

Table I lists parameter values for a few selected pressures.

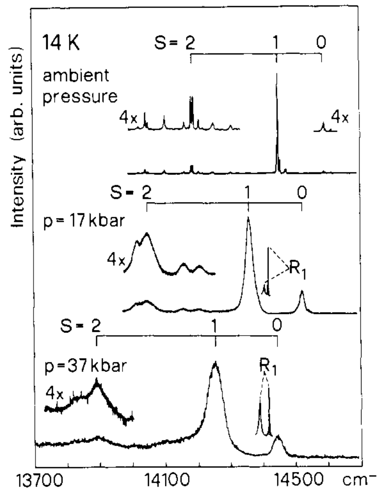

Figure 1. Luminescence spectra (14 K) of $\{triol\}(ClO_4)_3$ at three selected pressures. The lines denoted R_1 arise from the sapphire anvils (sharper line) and the ruby chips (broader line), which were added for pressure calibration. The purely electronic transitions to the ground-state dimer levels S = 0, 1, and 2 are indicated.

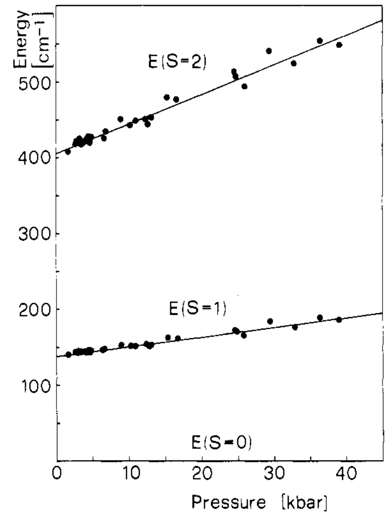

Figure 2. Ground-state exchange splitting as a function of hydrostatic pressure for $\{triol\}(ClO_4)_3$ at 14 K. The lines were obtained by a linear regression through the data points.

Table I. Exchange Parameters as a Function of Hydrostatic Pressure

$\{triol\}(ClO_4)_3$			$\{rhodo\}Cl_5{\cdot}H_2O$		
P, kbar	J, cm^{-1}	j, cm^{-1}	P, kbar	J, cm^{-1}	j, cm^{-1}
0	−64.0	1.6	0	−15.2	0.16
9	−72.3	1.2	9.5	−16.4	0.16
25	−82.6	0.8	25	−18.8	0.3
39	−87.8	1.6	42	−21.4	0.3

The observed effects in $\{rhodo\}Cl_5{\cdot}H_2O$ are similar, the energy shifts being somewhat smaller because the exchange coupling is weaker. The emitting dimer state in this complex is a spin quintet, and the observed transitions are $S^* = 2 \rightarrow S = 1$, 2, and 3.[5] As for $\{triol\}^{3+}$, the exchange splittings increase linearly with pressure. Exchange parameters are listed for a few selected pressures in Table I.

We obtain the following pressure dependences of the bilinear exchange parameter J for the two complexes:

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(1) Riesen, H.; Güdel, H. U. *J. Chem. Phys.*, in press.

(2) Riesen, H.; Kindler, U.; Güdel, H. U. *Rev. Sci. Instrum.*, in press.

(3) Riesen, H.; Güdel, H. U.; Chaudhuri, P.; Wieghardt, K. *Chem. Phys. Lett.* **1984**, *110*, 552.

(4) Riesen, H.; Güdel, H. U. *Mol. Phys.*, in press.

(5) Riesen, H.; Güdel, H. U. *Mol. Phys.* **1986**, *58*, 509.