thermodynamically most stable among all the equilibrating organorhodium(III) complexes. The formation of **2a**, therefore, slows the rate of the formation of benzyl chloride. In the general case, the acid chloride structure determines the relative stabilities of **1**–**3**. Thus, **2** is the most stable complex when R = benzyl or methyl (or alkyl in general),[17a] whereas **3** is the most stable complex when R = Ph, PhCH=CH, or CH_2Cl.[9,10a,17a] The effect of acid chloride structure on relative stabilities of these organorhodium(III) complexes and the barriers between them are small, however, compared to the effect of acid chloride structure on the barrier to the formation of decarbonylation products (alkyl or aryl chloride and olefin). For example, labeled acid chlorides $R^{13}COCl$ are formed from reactions of RCOCl (acetyl, butanoyl, cinnamoyl, benzoyl, and phenylacetyl chlorides, among others) with $RhCl(CO)(PPh_3)_2$ in the presence of ^{13}CO; decarbonylation products are not formed in significant amounts in competition with the labeling except for benzyl chloride.[3] The labeling of the acid chlorides RCOCl involves an excursion through the equilibrating organorhodium(III) complexes, but only benzyl substitution greatly reduces the barrier to the formation of decarbonylation product.

(4) Kinetic studies of reductive eliminations of *p*-chlorobenzyl chloride and methyl chloride from corresponding Rh(III) complexes have been reported.[9a,18] In general, these kinetic studies were carried out by monitoring the first-order disappearance of the corresponding Rh(III) complex without analyzing for the product *p*-chlorobenzyl chloride or methyl chloride. As we have just discussed, this decarbonylation reaction is a complex system of a set of equilibrating organorhodium(III) complexes. It needs more rigorous treatment than simple first-order approximations.

In summary, this kinetic study of the decarbonylation of phenylacetyl chloride gives us a clear picture of this decarbonylation system. We now have a better understanding of the various experimental observations on the general decarbonylation reaction. To establish mechanisms for this product formation step, we need more information from experiments other than kinetic measurements. We are continuing to investigate full details in the product formation step in decarbonylation reactions.

---

[18] Weinberg, E. L.; Baird, M. C. *J. Organomet. Chem.* **1979**, *179*, C61–C64.

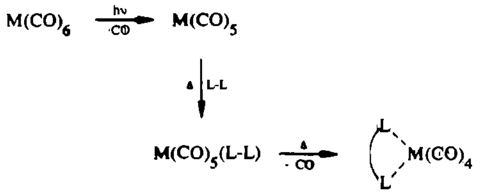
Contribution from the School of Chemical Sciences,
The National Institute for Higher Education,
Glasnevin, Dublin 9, Ireland

(μ-4,4′-Dimethyl-2,2′-bipyridine)bis(pentacarbonylchromium): Isolation and Reactivity of a Novel Complex Relevant to Group 6 Metal Tetracarbonyl Chelate Formation

Bernadette S. Creaven, Friedrich-Wilhelm Grevels,[1]
and Conor Long*

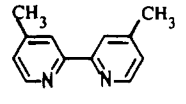
Received November 2, 1988

The photochemical formation of chelate $M(CO)_4(L\text{-}L)$ complexes from group 6 metal hexacarbonyls and bidentate ligands (L-L), such as 2,2′-bipyridine derivatives and other diimine type ligands, is a matter of current mechanistic investigations.[2-8] The formation of the chelate product is thought to occur subsequent to the photochemical generation of the $M(CO)_5(L\text{-}L)$ species, in which the ligand L-L is coordinated in a monodentate fashion (eq 1). Spectral characterization of $M(CO)_5(L\text{-}L)$ and kinetic data for its conversion into $M(CO)_4(L\text{-}L)$ have been obtained from FTIR[2] and UV–vis photodiode-array spectroscopy[3-7] and from laser flash-photolysis experiments.[8] However, it should be noted that in these experiments the $M(CO)_5(L\text{-}L)$ species were generated in situ in the presence of a large excess of L-L, which may influence the kinetics of the system. The IR spectroscopic identification of $M(CO)_5(L\text{-}L)$ was based on the similarity of the CO stretching vibrational pattern to that of the model compounds $M(CO)_5$(2-phenylpyridine).[2] Recently, several monodentate $M(CO)_5(L\text{-}L)$ complexes with L-L ligands such as 1,8-diazabiphenylene,[6] dipyridylalkane,[9] and ethylenediamine[10] have been isolated. However, these ligands do not have the same, if any, propensity to form chelate complexes as do 2,2′-bipyridines and other diimine type derivatives.



(1)

Therefore, we attempted the synthesis and isolation of a monodentately coordinated $Cr(CO)_5(L\text{-}L)$ complex, utilizing 4,4′-dimethyl-2,2′-bipyridine (dmbpy) as the L-L ligand and pentacarbonyl(η^2-(*Z*)-cyclooctene)chromium[11] as a source of the $Cr(CO)_5$ unit. The principal aim of this investigation was to monitor the kinetics of $Cr(CO)_4(L\text{-}L)$ formation in the absence of free bipyridine ligand. However, unexpectedly the product we isolated contained, not one, but two $Cr(CO)_5$ units per dmbpy ligand.



dmbpy

Experimental Section

Equipment and Materials. All solvents used in the syntheses and spectroscopic measurements were purified and deoxygenated by standard techniques.[12] Hexacarbonylchromium and 4,4′-dimethyl-2,2′-bipyridine were purchased from Strem Chemicals and Aldrich, respectively, and used as received. $Cr(CO)_5(\eta^2\text{-}(Z)\text{-cyclooctene})$[11] and $Cr(CO)_4$(dmbpy)[5] were prepared according to the published procedures. Infrared spectra, with band positions accurate to ±3 cm^{-1}, were recorded on a Perkin-Elmer 983G instrument in nitrogen-purged solutions, using a cell with sodium chloride windows and $d = 0.1$ mm. UV–vis spectra, with ±2-nm wavelength accuracy, were obtained by means of a Hewlett-Packard 8452A diode-array spectrophotometer fitted with a ChemStation data station. Elemental analyses were conducted by the Microanalytical Laboratory, University College, Dublin.

Acquisition and Treatment of UV–Vis Spectroscopic Data. Solutions for recording UV–vis spectra were prepared by placing a sample of the solid complex **1** in a quartz cuvette ($d = 1$ cm) attached to a bulb containing the solvent. The solvent was degassed by three freeze–pump–thaw cycles and transferred in vacuo to the cuvette. The initial spectrum was obtained as soon as the solid had dissolved, usually within 1 min after adding the solvent. Each spectrum, which took 0.1 s to acquire, was measured five times. This allowed the absorbance to be determined to ±0.001 absorbance units. When the grow-in of the band of **2** at 518 nm was monitored, the actual monitoring wavelength was 510 nm, but the absorbance at 690 nm was subtracted from the absorbance at 510 nm in order to reduce the effect of light scattering and lamp intensity variations in the single-beam instrument. Kinetic parameters

---

[1] Present address: Max-Planck-Institut für Strahlenchemie, Stiftstrasse 34-36, D-4330 Mülheim a.d. Ruhr, Fereral Republic of Germany.

[2] Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 5784–5786.

[3] Schadt, M. J.; Gresalfi, N. J.; Lees, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 506–508.

[4] Schadt, M. J.; Gresalfi, N. J.; Lees, A. J. *Inorg. Chem.* **1985**, *24*, 2942–2946.

[5] Schadt, M. J.; Lees, A. J. *Inorg. Chem.* **1986**, *25*, 672–677.

[6] Marx, D. E.; Lees, A. J. *Inorg. Chem.* **1987**, *26*, 620–622.

[7] Chan, L.; Lees, A. J. *J. Chem. Soc.*, Dalton *Trans.* **1987**, 513–517.

[8] Kalyanasundaram, K. *J. Phys. Chem.* **1988**, *92*, 2219–2223.

[9] Marx, D. E.; Lees, A. J. *Organometallics* **1986**, *5*, 2072–2074.

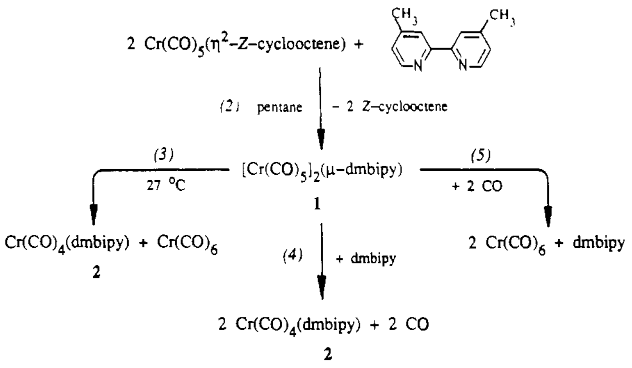
[10] Marx, D. E.; Lees, A. J. *Inorg. Chem.* **1987**, *26*, 2254–2257.

[11] Grevels, F.-W.; Skibbe, V. *J. Chem. Soc., Chem. Commun.* **1984**, 681–683.

[12] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1980.

0020-1669/89/1328-2231$01.50/0

Scheme I. Reactions 2-5



were calculated by using Hewlett-Packard kinetics software, which utilizes a curve-fitting routine for first-order kinetics. The observed data were fitted to the expression $A = a_1 + a_2e^{-kt}$, where A is the absorbance at time t, a_1 and a_2 are constants related to the initial and final absorbances at the monitoring wavelength, and k is the observed first-order rate constant (k_{obs}).

Preparation of (μ-4,4′-Dimethyl-2,2′-bipyridine)bis(pentacarbonylchromium) (1). A solution of 4,4′-dimethyl-2,2′-bipyridine (0.20 g, 1.09 mmol) in pentane (10 mL) was added to solid $Cr(CO)_5(\eta^2\text{-}(Z)\text{-cyclooctene})$ (0.27 g, 0.89 mmol) under a dry nitrogen atmosphere at ambient temperature, and the mixture was stirred. Upon dissolving of the solid $Cr(CO)_5(\eta^2\text{-}(Z)\text{-cyclooctene})$, the color of the solution changed from light yellow to orange, and shortly thereafter crystalline **1** precipitated. The crystals were collected by filtration, washed repeatedly with cold pentane to remove the Z-cyclooctene and excess dmbpy, and dried in vacuo. Yield: 0.24 g of **1** (93%) as orange crystals. Anal. Calcd for $C_{22}H_{12}Cr_2N_2O_{10}$: C, 46.5; H, 2.1; N, 4.9. Found: C, 46.2; H, 2.2; N, 4.6. Although solid **1** is stable at ambient temperature in air, it was stored under nitrogen atmosphere at −20 °C.

Results

The transformations observed in this study are summarized in Scheme I. Crystalline product **1** is readily isolated in a pure state in reaction 2, Scheme I. The IR spectrum of **1** in toluene solution exhibits four bands in the CO stretching vibrational region at 2068 (w), 1937 (st), 1921 (st), and 1905 (m) cm^{-1} (Figure 1A); an additional band at 1983 cm^{-1} is assigned[13] to a small amount of $Cr(CO)_6$ formed upon decomposition of **1** (vide infra). Three infrared-active CO stretching vibrational modes are expected for a square-pyramidal $M(CO)_5$ moiety, these being the A_1(w), E(st), and A_1(m) modes.[14] However, depending on the nature of the ligand attached to the pentacarbonylmetal fragment, the C_{4v} local symmetry may be severely perturbed. In such cases the formally forbidden B_2 mode gains some intensity and, in addition, the degeneracy of the E mode may be lifted. Such effects have been observed in the IR spectra of various $M(CO)_5(\eta^2\text{-olefin})$ complexes.[11,15] Thus, on the basis of the infrared spectral data alone, one could assign the formula $Cr(CO)_5(dmbpy)$ to complex **1**. Furthermore, the UV–vis spectrum with a lowest energy maximum at λ = 410 nm (Figure 3A) would also be consistent with this assignment.

However, the elemental analysis of **1** quite unexpectedly reveals that *two* $Cr(CO)_5$ units, instead of one, are coordinated to the dmbpy ligand.[16] This composition, $[Cr(CO)_5]_2(dmbpy)$, is surprising as, in the preparation of **1**, the dmbpy ligand has been added in a 1.2-fold molar excess over the $Cr(CO)_5$(olefin) complex.

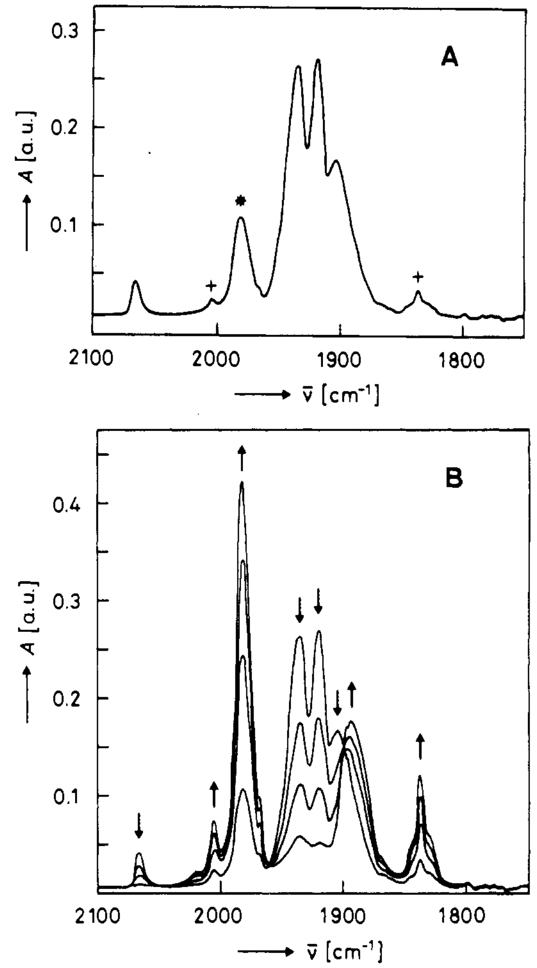


Figure 1. (A) CO stretching vibrational pattern in the infrared spectrum of **1** (3.1×10^{-3} mol L^{-1}) in toluene solution. The ✱ and + marks indicate the presence of some $Cr(CO)_6$ and $Cr(CO)_4$(dmbpy) formed following the dissolution of **1**. (B) Spectral changes occurring upon standing of the solution for 1500, 3600, and 6960 s at ambient temperature, indicating the formation of **2** and $Cr(CO)_6$ in 1:1 molar ratio.

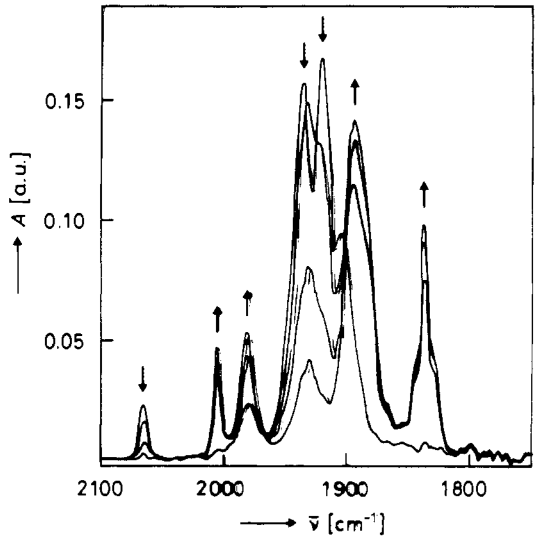


Figure 2. Infrared spectral changes in the CO stretching vibrational region occurring upon standing of a solution of **1** (1.8×10^{-3} mol L^{-1}) and dmbpy (0.13 mol L^{-1}) in toluene at ambient temperature for 900, 2220, and 11520 s. Note that the yield of **2**, compared with that in Figure 1B, is increased while the yield of $Cr(CO)_6$ is reduced.

The intensity of the IR bands of **1** diminished upon allowing the toluene solution to stand at ambient temperature (Figure 1B). Concomitant growth of new features at 2007 (w), 1896 (st), and 1839 (m) cm^{-1} is attributed to the formation of the $Cr(CO)_4$(dmbpy) chelate complex (**2**). A further strong band at 1983 cm^{-1} indicates the simultaneous formation of $Cr(CO)_6$ according to reaction 3, Scheme I. The maintenance of isosbestic points throughout these changes in the infrared spectra indicates that

---

(13) It is possible that this band hides the normally infrared-forbidden B_2 mode of the $Cr(CO)_5$ complex **1**, which eventually may be weakly active.

(14) Braterman, P. S. *Metal Carbonyl Spectra*; Academic: London, 1975.

(15) Skibbe, V. Doctoral Dissertation, Universität Duisburg, 1985.

(16) A preliminary X-ray diffraction analysis of the molecular structure of **1** reveals an angle close to 90° between the two pyridine rings. Creaven, B. S.; Howie, R. A.; Long, C.; Low, J.; McQuillan, G. P. *Inorg. Chim. Acta* **1989**, *157*, 151–152.

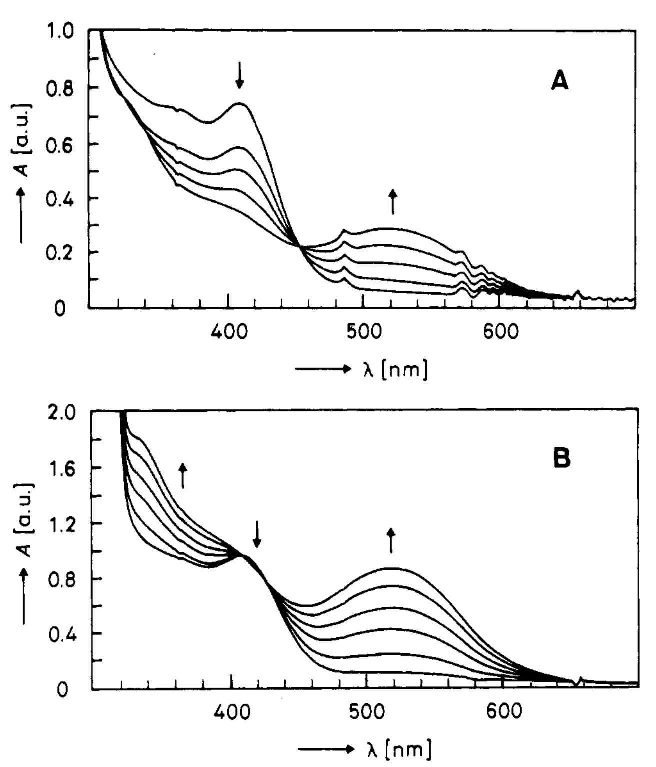


Figure 3. (A) UV–vis spectrum of a solution of **1** (1.2×10^{-4} mol L^{-1}) in toluene and the spectral changes occurring upon standing of the solution at 23 °C for 500, 1250, 2250, and 4000 s. (B) UV–vis spectral changes occurring upon standing of a solution of **1** (1.4×10^{-4} mol L^{-1}) and dmbpy (0.13 mol L^{-1}) in toluene at 23 °C for 150, 375, 675, 1000, 1550, and 3775 s.

the process is uncomplicated by side or subsequent reactions. Moreover, we note that the ratio of $Cr(CO)_4(dmbpy)$ (**2**) to $Cr(CO)_6$ remains constant during the course of the reaction. Having determined the extinction coefficients of $Cr(CO)_6$ at 1983 cm^{-1} (ϵ = 14 500 L mol^{-1} cm^{-1}), of **2** at 1839 cm^{-1} (ϵ = 3670 L mol^{-1} cm^{-1}), and of **1** at 2068 cm^{-1} (ϵ = 1250 L mol^{-1} cm^{-1}) in toluene solution, we confirmed the quantitative nature of the reaction, with formation of the two products in 1:1 molar ratio according to the stoichiometry indicated in reaction 3, Scheme I. The above infrared bands are chosen because of minimal overlap between the various components in the reaction mixtures.

We examined the effect of added dmbpy on the transformation of **1** into **2**. The spectral changes observed in the presence of a 70-fold excess of dmbpy are presented in Figure 2. In this case the yield of $Cr(CO)_4(dmbpy)$ (**2**) is increased, relative to that in the absence of excess dmbpy, at the expense of $Cr(CO)_6$ formation (cf. Figure 1B). This indicates that under these conditions reaction 4 in Scheme I makes an essential contribution to the overall stoichiometry.

Photodiode-array spectroscopy was used to obtain UV–vis spectra. In degassed toluene solution the spectrum of **1** (Figure 3A) exhibits a maximum at 410 nm (ϵ = 5150 L mol^{-1} cm^{-1}).[17] The intensity of this absorption diminishes with time, while concomitant growth of a new band with λ_{max} = 518 nm is observed. The final spectrum is identical, in the visible region, with that obtained with an authentic sample of $Cr(CO)_4(dmbpy)$[5] (**2**). The rate of grow-in of the band at 518 nm follows first-order kinetics, providing an estimate of $k_{obs} = 3.3 \times 10^{-4}$ s^{-1} at 23 °C. Arrhenius plots of k_{obs} over the temperature range from 23 to 36 °C allows an estimate of E_a = +110 kJ mol^{-1} for the formation of $Cr(CO)_4(dmbpy)$ (**2**). From an Eyring plot ΔS^{*} = +51 J K^{-1} mol^{-1} is obtained. Addition of free dmbpy to the solution increases k_{obs} at ambient temperature to a maximum value of 1.2×10^{-3} s^{-1} (Figure 4). Furthermore, the intensity of the band of product **2** at 518 nm, relative to that of complex **1** at 410 nm, is almost doubled upon the addition of excess dmbpy (Figure 3B). This observation is in accord with the IR spectroscopic results, thus confirming that in the presence of a large excess of free dmbpy the reaction in essence follows the stoichiometry of reaction 4, Scheme I.

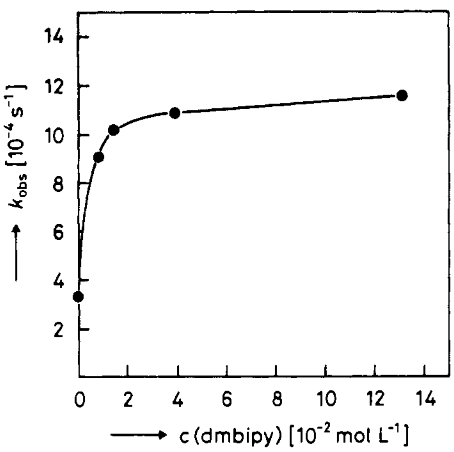


Figure 4. Plot of the observed first-order rate constant (k_{obs}) for the formation of **2** from **1** against the concentration of added dmbpy.

Saturation of the toluene solvent with carbon monoxide prior to dissolving complex **1** results in a more rapid disappearance of the band at 410 nm, yielding $k_{obs} = 2.8 \times 10^{-3}$ s^{-1}. Only a small yield of $Cr(CO)_4(dmbpy)$ (**2**), which appears with $k_{obs} = 3.0 \times 10^{-3}$ s^{-1}, is detected under these conditions, viz., <20% of that obtained in the absence of both carbon monoxide and free dmbpy. This implies that both $Cr(CO)_5$ units of complex **1** can dissociate and subsequently take up CO to form $Cr(CO)_6$ (reaction 5 in Scheme I).

Discussion

These results are reasonably accommodated by the sequence of reactions displayed in eq 6a–d. We suggest a (reversible)

$$[Cr(CO)_5]_2(\mu\text{-dmbpy}) \rightleftarrows Cr(CO)_5(dmbpy) + Cr(CO)_5 \quad (6a)$$

$$Cr(CO)_5(dmbpy) \rightleftarrows dmbpy + Cr(CO)_5 \quad (6b)$$

$$Cr(CO)_5(dmbpy) \rightarrow \underset{\mathbf{2}}{Cr(CO)_4(dmbpy)} + CO \quad (6c)$$

$$Cr(CO)_5 + CO \rightarrow Cr(CO)_6 \quad (6d)$$

dissociation of one $Cr(CO)_5$ unit from **1** to be the initial step (eq 6a). The resulting $Cr(CO)_5(dmbpy)$ species subsequently may undergo chelate ring closure with formation of **2** and extrusion of carbon monoxide, which should be the rate-determining step (eq 6c). This latter assumption would be consistent with the observed activation parameters. The competitive further dissociation of $Cr(CO)_5(dmbpy)$ (eq 6b) does not play a significant role, unless the resulting $Cr(CO)_5$ species is efficiently captured by CO (eq 6d). Thus, in CO-saturated solution not only is the disappearance of **1** greatly accelerated by preventing recoordination of the first liberated $Cr(CO)_5$ unit but also the yield of $Cr(CO)_6$ (at the expense of chelate complex **2** formation) increases markedly. Likewise, the presence of excess dmbpy accelerates the disappearance of **1** by capturing the $Cr(CO)_5$ unit lost in the first step (eq 6a). However, in this case the dissociation of $Cr(CO)_5(dmbpy)$ according to the equilibrium in eq 6b is largely suppressed, thus increasing the stationary concentration of this monodentate species and, consequently, favoring the formation of the chelate $Cr(CO)_4(dmbpy)$ complex **2**. The lability of $Cr(CO)_5(dmbpy)$ (eq 6b) seems to contrast with the behavior of the related tungsten complex $W(CO)_5[4,4'\text{-}(n\text{-}C_{19}H_{39})_2\text{-}2,2'\text{-bpy}]$, which was reported[2] not to yield an appreciable amount of $W(CO)_6$, even in the presence of ca. 10^{-3} mol L^{-1} carbon monoxide. However, it should be noted that this latter result was obtained in the presence of an excess of the 4,4'-dialkyl-2,2'-bipyridine ligand.

---

(17) This extinction coefficient is evaluated from UV–vis spectral changes observed upon complete conversion of **1** into **2** by assuming that the stoichiometry follows eq 3 and utilizing ϵ = 3660 L mol^{-1} cm^{-1} for complex **2** at 518 nm.

Unfortunately, because of the presumed UV-vis and IR spectral similarities between **1** and $\mathrm{Cr(CO)_5}$(dmbpy), it was not possible to unambiguously identify the latter in the reaction mixtures and to separate the individual rate constants for the dissociation of either **1** or $\mathrm{Cr(CO)_5}$(dmbpy). Nevertheless, we are aware that $\mathrm{Cr(CO)_5}$(dmbpy) may be present in significantly high stationary concentrations, particularly in those experiments where large amounts of free dmbpy ligand were added.[18] Therefore, the significance of the k_{obs} values obtained under the various conditions described above is ambiguous at the present stage. Further experiments with various concentrations of CO and dmbpy are necessary in order to obtain kinetic data from which the individual rate constants of all the processes in eq 6a,b can be obtained.

Concluding Remarks

To our knowledge a dinuclear complex of type **1** has not been considered previously to be involved in the formation of group 6 $\mathrm{M(CO)_4}$(L-L) chelate complexes with 1,4-diazadiene type ligands. Moreover, **1** appears to be the first example of a complex in which such a ligand acts as a bridge between two separate transition-metal centers. Naturally the question arises whether or not the formation and isolation of **1** is a unique case in this context. We are currently extending our studies to other, related, chelating ligands and to the analogous molybdenum and tungsten compounds in order to clarify this point.

A plausible explanation for the high-yield isolation of **1** is that its precipitation from pentane solution, owing to the low solubility in that solvent, drives the equilibrium of eq 6a to the left side. Beyond this it seems possible that upon coordination of one $\mathrm{Cr(CO)_5}$ unit to the dmbpy ligand the coordinating ability of the second pyridine ring is enhanced. It is worthwhile to mention in this context that in some cases of polydentate N-donor heteroaromatic ligands it was found difficult to obtain only partly coordinated complexes because of the propensity of such ligands toward complexation of all available coordination sites.[19] However, on the other hand it has to be noted that in complex **1**, as shown by the X-ray diffraction structure analysis[16] of the crystalline material, the two pyridine rings are twisted by ca. 90° relative to each other, which prevents any interaction through the π system. Thus, provided that this structural feature is maintained in solution, mutual influence between the two halves of complex **1** should be restricted to through-space interactions and to transmission through the σ system of the dmbpy ligand.

Registry No. 1, 120360-44-3; **2**, 15740-68-8; dmbpy, 1134-35-6; $\mathrm{Cr(CO)_5}$(η^2-(*Z*)-cyclooctene), 92889-73-1; $\mathrm{Cr(CO)_6}$, 13007-92-6; CO, 630-08-0.

---

(18) Comparing the IR spectral changes displayed in Figures 1B and 2, we note that in the latter case the splitting of the strong bands at 1937 and 1921 cm^{-1} is not maintained throughout but that a band at an intermediate position emerges. This observation may be taken as pointing toward the presence of $\mathrm{Cr(CO)_5}$(dmbpy) in which, by analogy with the model compound $\mathrm{Cr(CO)_5}$(2-phenylpyridine),[2] the E-mode degeneracy could perhaps be preserved.

(19) Ernst, S.; Kaim, W. *Inorg. Chim. Acta* **1988**, *144*, 223-226 and references cited therein.

Contribution from the Laboratoire de Chimie
de Coordination du CNRS, 205,
route de Narbonne, 31077 Toulouse Cedex, France

New Pathway to Heterodinuclear Complexes with Equivalent Coordination Sites: Application of the Cis-Trans Isomerization of the Oxamido Group

J.-P. Costes* and J.-P. Laurent

Received October 7, 1988

There are several research fields in which it would be advantageous to have a series of well-characterized mixed-metal complexes. From a literature survey, it appears that there are mainly two types of ligands that can simultaneously coordinate two metal ions. In the first type the two coordination sites are equivalent, while they are inequivalent in the second. The coordination site inequality favors the formation of mixed-metal complexes and a large majority of the known heterodinuclear complexes have been obtained in this way; the most frequent situation involves N_2O_2 and O_4 coordination sites.[1-3] To our knowledge, only two series of heterodinuclear complexes with identical coordination sites for both metal ions have been prepared so far. In the first case,[4] mononuclear complexes of β,δ-triketones or β-ketophenols have been used as ligands toward a second metal ion to yield heterodinuclear compounds. The interest of this strategy is limited by the instability of the mononuclear precursors, which very often transform into the related homodinuclear species even at room temperature. The second series[5,6] involves the Robson macrocyclic binucleating ligand, which offers equivalent N_2O_2 coordination sites to both metal ions. These heterodinuclear complexes (Cu(II)/M(II) with M = Mn, Co, Fe) have been prepared by a stepwise synthesis that includes a dinuclear intermediate with dissimilar surroundings for the metal ions. The coordination site equality is achieved by a modification of the ligand in the last step of the synthesis.

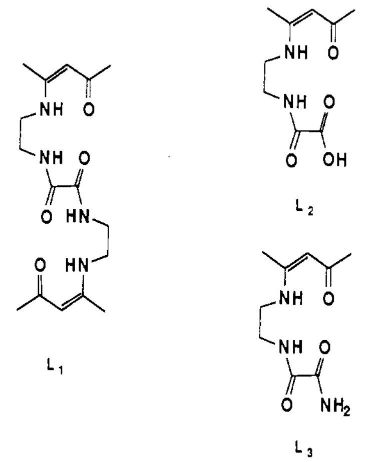


Figure 1. Ligands.

In the present paper we report on a new ligand, *N,N′*-bis(4-methyl-5-aza-3-hepten-2-on-7-yl)oxamide (L_1; cf. Figure 1), which can be isolated in the free state and then reacted with a copper ion to yield a mononuclear complex, $[\mathrm{Cu}(L_1\text{-}3\mathrm{H})]^-$, which is able to act as a ligand toward a second divalent ion M^{2+} to yield a heterodinuclear species $\mathrm{Cu}(L_1\text{-}4\mathrm{H})\mathrm{M}$ (L_1-3H and L_1-4H representing the tri- and tetradeprotonated forms of L_1, respectively).

The possibility of preparing a mixed-metal complex with equivalent surrounding for both metal ions from a preformed symmetrical binucleating ligand is unexpected. It relies on the possibility of changing the conformation (cis vs trans) of the oxamido group. Indeed we could demonstrate that in the mononuclear species the copper ion is actually surrounded by three nitrogen and one oxygen atoms while both metals have N_2O_2 surrounding in the mixed-metal (Cu/Ni) complex.

Experimental Section

Ligand L_1. To a stirred solution of diethyl oxalate (2.6 g, 17.6 mmol) in CH_2Cl_2 (50 cm^3) was added AEH,[7] 7-amino-4-methyl-5-aza-3-hep-

---

(1) Casellato, U.; Vigato, P. A.; Vidali, M. *Coord. Chem. Rev.* **1977**, *23*, 31.
(2) Groh, S. E. *Israel J. Chem.* **1976-77**, *15*, 277.
(3) Casellato, U.; Vigato, P. A.; Fenton, D. E.; Vidali, M. *Chem. Soc. Rev.* **1979**, *8*, 199.
(4) Casellato, U.; Tamburini, S.; Vigato, P. A.; De Stefani, A.; Vidali, M.; Fenton, D. E. *Inorg. Chim. Acta* **1983**, *69*, 45.
(5) Gagne, R. R.; Spiro, C. L. *J. Am. Chem. Soc.* **1980**, *102*, 1443.
(6) Lambert, S. L; Spiro, C. L.; Gagne, R. R.; Hendrickson, D. N. *Inorg. Chem.* **1982**, *21*, 68.
(7) Cros, G.; Costes, J.-P. *C. R. Seances Hebd. Acad. Sci., Ser. 2* **1982**, *294*, 173.

0020-1669/89/1328-2234$01.50/0