Articles

Pentacarbonyl(1,4-diisopropyl-1,4-diazabutadiene)chromium: Isolation and Reactivity of the Monodentate Intermediate en Route to Cr(CO)4(iprop-DAB) Chelate Ring Closure

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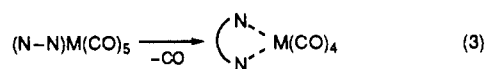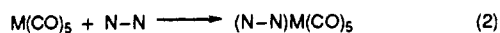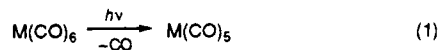Middle East Technical University, 06531 Ankara, Turkey*

Exchange of the olefin ligand in $Cr(CO)_5(\eta^2\text{-}(Z)\text{-cyclooctene})$ by 1,4-diisopropyl-1,4-diazabutadiene (iprop-DAB) yields $Cr(CO)_5(\text{iprop-DAB})$ (**1**), where the potentially bidentate DAB ligand coordinates in a monodentate fashion. Complex **1** is isolated as red crystals and fully characterized (elemental analysis, IR, UV−vis, ^1H NMR and ^{13}C NMR spectra). In hydrocarbon solution at ambient temperature it decays via two competitive routes involving (a) chelate ring closure with CO extrusion to form $Cr(CO)_4(\text{iprop-DAB})$ (**2**) and (b) loss of the iprop-DAB ligand and takeup of CO to form $Cr(CO)_6$, as monitored by means of NMR, UV−vis, and IR spectroscopy. Favorable conditions for the chelate ring closure leading to **2** are the high concentration of **1**, the presence of added iprop-DAB, and the absence of CO, while the opposite is true for the formation of $Cr(CO)_6$. The decay of **1** is retarded in the presence of increasing amounts of added iprop-DAB. It essentially follows pseudo-first-order kinetics with k_{obs} approaching a lower limiting value of 2.7×10^{-5} s^{-1} under Ar at 23 °C, whereby $Cr(CO)_4(\text{iprop-DAB})$ (**2**) and $Cr(CO)_6$ are formed in a ca. 20:1 ratio. Experiments at variable temperature yield $\Delta H^{\ddagger} = 48 \pm 6$ kJ mol^{-1} and $\Delta S^{\ddagger} = -170 \pm 18$ J K^{-1} mol^{-1}. In the presence of added CO or (E)-cyclooctene (ECO) the decay of **1** is accelerated, whereby additional $Cr(CO)_6$ or $Cr(CO)_5(\eta^2\text{-ECO})$ are formed at the expense of $Cr(CO)_4(\text{iprop-DAB})$ (**2**) production. Complementary studies involving continuous irradiation of $Cr(CO)_6$ and iprop-DAB indicate that photogenerated **1** subsequently undergoes photolytic CO dissociation with formation of **2** in addition to the thermal chelate ring closure.

Introduction

Photolysis of group 6 metal hexacarbonyls in the presence of potentially bidentate diimine type ligands N−N (1,4-diazabutadienes, 2,2′-bipyridines, or pyridine-2-carbaldehyde imines) ultimately results in the formation of the respective $M(CO)_4(N-N)$ chelate complexes.[1,2] This process reportedly involves the initial photosubstitution of one CO group, leading to an intermediate product of type $M(CO)_5(N-N)$, in which the N−N ligand is coordinated in a monodentate fashion, eqs 1 and 2. It has received attention from several investigators who studied the subsequently occurring chelate ring closure with extrusion of the second CO group, eq 3.

In most of these studies the $M(CO)_5(N-N)$ intermediate has been photogenerated in situ from $M(CO)_6$ in the presence of excess N−N ligand, using either short-time, continuous irradiation,[3−11] or laser flash excitation.[12,13]

$$M(CO)_6 \xrightarrow[-CO]{h\nu} M(CO)_5 \tag{1}$$

$$M(CO)_5 + N-N \longrightarrow (N-N)M(CO)_5 \tag{2}$$

$$(N-N)M(CO)_5 \xrightarrow{-CO} \left(\begin{smallmatrix} N \\ N \end{smallmatrix} \right) M(CO)_4 \tag{3}$$

FTIR[3,10] and UV−vis[4−13] detection were employed for the spectral characterization of the $M(CO)_5(N-N)$ species and for monitoring the conversion into the respective $M(CO)_4(N-N)$ chelate product. This way a large body of kinetic data and activation parameters have been accumulated, including volumes of activation[11]

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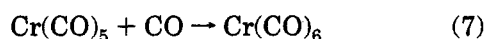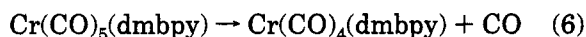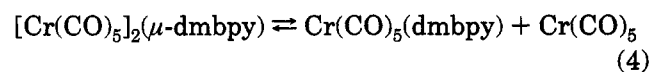[®] Abstract published in *Advance ACS Abstracts*, June 1, 1994.
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from variable-pressure experiments. However, in only one case (N—N = ethylenediamine) could the monodentate $M(CO)_5(N—N)$ type of complex be isolated from the irradiated solution.[14] As an alternative approach in situ photogenerated $M(CO)_5(THF)$ was used as a source of the $M(CO)_5$ unit, which upon reaction with diimine type ligands in the dark yielded the desired $M(CO)_5(N—N)$ products,[7,15,16] some of which could be isolated.[7,15] However, in those cases the isolated compounds showed little, if any, propensity to undergo chelate ring closure.

Following a similar strategy, we utilize (Z)-cyclooctene (ZCO) as a weakly bound stand-in ligand, which has the advantage that its $Cr(CO)_5$ complex is readily accessible on a preparative scale as a pure, crystalline substance. The solid material is stable enough for handling at ambient temperature, while in solution $Cr(CO)_5(\eta^2\text{-}ZCO)$ is rather labile and thus serves as a versatile source of the $Cr(CO)_5$ unit.[17] As a surprising result it was found that the reaction with 4,4'-dimethyl-2,2'-bipyridine (dmbpy) yields the dinuclear product $[Cr(CO)_5]_2(\mu\text{-}dmbpy)$[18,19] instead of the expected $Cr(CO)_5(dmbpy)$, although the latter species presumably is present in solution as one component of the system. At ambient temperature the decay occurs with formation of $Cr(CO)_4(dmbpy)$ and $Cr(CO)_6$ in 1:1 molar ratio, as determined by quantitative IR spectroscopy.[18] Substantial changes in both the product ratio and the decay kinetics are observed in the presence of added free dmbpy ligand or under a CO atmosphere. The expanded reaction scheme, eqs 4–7, takes these findings into account.

$$[Cr(CO)_5]_2(\mu\text{-}dmbpy) \rightleftharpoons Cr(CO)_5(dmbpy) + Cr(CO)_5 \quad (4)$$

$$Cr(CO)_5 + dmbpy \rightleftharpoons Cr(CO)_5(dmbpy) \quad (5)$$

$$Cr(CO)_5(dmbpy) \rightarrow Cr(CO)_4(dmbpy) + CO \quad (6)$$

$$Cr(CO)_5 + CO \rightarrow Cr(CO)_6 \quad (7)$$

As a continuation of these studies we have investigated a related system, which involves a diazabutadiene ligand, 1,4-diisopropyl-1,4-diazabutadiene (iprop-DAB), instead of the bipyridine derivative. In this paper we wish to report on the characterization and reactivity of the monodentate $Cr(CO)_5(iprop\text{-}DAB)$ complex (1).
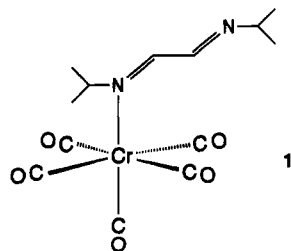
Results and Discussion

Continuous irradiation of $Cr(CO)_6$ and 1,4-diisopropyl-1,4-diazabutadiene (iprop-DAB) in alkane solution re-

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(19) Creaven, B. S.; Long, C.; Howie, R. A.; McQuillan, G. P.; Low, J. *Inorg. Chim. Acta* **1989**, *157*, 151–152.

sults in nearly quantitative conversion into the $Cr(CO)_4$-(iprop-DAB) chelate complex 2, eq 8, thus providing

$$Cr(CO)_6 \xrightarrow[-2CO]{h\nu/iprop\text{-}DAB} \underset{\textbf{2}}{Cr(CO)_4(iprop\text{-}DAB)} \quad (8)$$
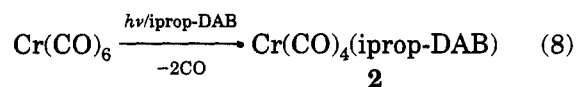
convenient access to this compound on a preparative scale. The monodentate $Cr(CO)_5(iprop\text{-}DAB)$ species (1) emerges as an intermediate product, as monitored by IR and UV—vis spectroscopy. However, exploratory experiments aiming at the accumulation and isolation of photogenerated 1 from such a solution were not very promising and discouraged us from making efforts in this direction on a preparative scale. Under various conditions of irradiation (vide infra) 1 remains a minor component of the reaction mixture. At any stage of conversion substantial amounts of $Cr(CO)_6$ and/or $Cr(CO)_4(iprop\text{-}DAB)$ (2) are present, which are difficult to separate from the thermally labile $Cr(CO)_5(iprop\text{-}DAB)$ (1).

In view of these problems it seemed advisable again to employ $Cr(CO)_5(\eta^2\text{-}ZCO)$ as a source of the $Cr(CO)_5$ unit and thus to attempt the synthesis of the desired $Cr(CO)_5(iprop\text{-}DAB)$ (1) under thermally mild conditions in the dark, eq 9. Indeed, ligand exchange occurs upon

$$Cr(CO)_5(\eta^2\text{-}ZCO) + iprop\text{-}DAB \rightarrow$$
$$\underset{\textbf{1}}{Cr(CO)_5(iprop\text{-}DAB)} + ZCO \quad (9)$$
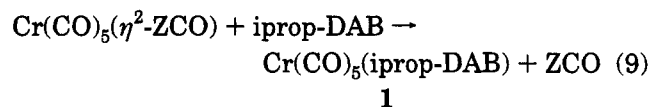
warming a cold n-hexane solution of $Cr(CO)_5(\eta^2\text{-}ZCO)$ and 1,4-diisopropyl-1,4-diazabutadiene to ≥ 0 °C. It takes ca. 15 min at ambient temperature to bring the exchange to completion, with only trace amounts of $Cr(CO)_6$ and chelate complex 2 detectable in the IR spectrum. Red crystals of pure $Cr(CO)_5(iprop\text{-}DAB)$ (1) precipitate upon immediate cooling to dry-ice temperature. In crystalline form this compound is stable enough for handling at ambient temperature, although temperatures below -20 °C are recommended for storing it over longer periods. Solutions of 1 should also be prepared and handled well below ambient temperature in order to avoid thermal decay.

Apart from the spectroscopic characterization, the identification of 1 rests on the elemental analysis, which shows that the isolated product contains only one $Cr(CO)_5$ unit attached to the iprop-DAB ligand, in contrast to the 2:1 composition of the previously reported dimethylbipyridine bis-$Cr(CO)_5$ complex.[18,19] In accordance with the unsymmetrical structure of the monodentate complex 1, both the ^1H- und ^{13}C-NMR spectra exhibit two sets of signals for the two different isopropyl groups, while the olefin protons in the ^1H-NMR spectrum appear as an AB system (cf. Figure 2A, Table 2). The IR spectrum expectedly shows a CO stretching vibrational pattern (Figure 1) consistent with the C_{4v} local symmetry of the $Cr(CO)_5$ skeleton [2067 (w, a_1), 1940 (st, e), and 1925 (m, a_1)]. The position of the characteristic maximum in the UV—vis spectrum at 405 nm (cf. Figure 3) compares well with previously reported data of the in situ photogenerated $Cr(CO)_5(N—N)$ complexes of iprop-DAB (402 nm, in benzene solution)[6] and other DAB ligands.[5,6]

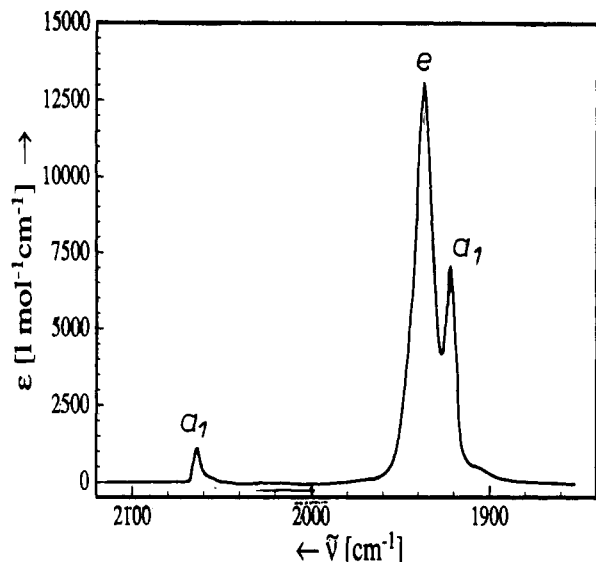Monitoring the thermal decay of 1 in solution at ambient temperature by means of NMR, IR, and UV—

Figure 1. CO stretching vibrational pattern in the IR spectrum of $Cr(CO)_5$(iprop-DAB) (1) [2067 (a_1), 1940 (e), and 1925 (a_1)] recorded in n-hexane immediately after dissolving.

vis spectroscopy reveals that in addition to the expected intramolecular chelate ring closure with formation of $Cr(CO)_4$(iprop-DAB) (2) varying amounts of $Cr(CO)_6$ are formed, depending on the reaction conditions.

Figure 2 illustrates the spectral changes observed in the olefin proton region of the ^{1}H-NMR spectrum, when a ca. 75 mM solution of 1 in methylcyclohexane-d_{14}, placed in a sealed NMR tube, is allowed to stand at ambient temperature.[20] The spectrum displayed in Figure 2A is recorded shortly after the cold solution has been warmed to 300 K. It is dominated by the two doublets associated with the AB system of 1, the integral of which accounts for 61% of the total intensity. Another pair of doublets, barely discernible (4%), is tentatively assigned as an isomeric species of 1, from which it may differ with respect to the orientation of the uncoordinated half of the iprop-DAB ligand (s-trans/s-cis conformation). The two singlets at 8.13 ppm (4%) and 7.79 ppm (19%) are readily identified as $Cr(CO)_4$-(iprop-DAB) (2) and free iprop-DAB, respectively, by comparison with the spectra of authentic samples. What remains to be discussed is the species associated with the signal at 8.74 ppm (11%). The singlet nature of this signal, along with the observation of only one set of lines associated with the isopropyl group (not shown in Figure 2), requires a symmetrical structure, for which the dinuclear compound $[Cr(CO)_5]_2$(μ-iprop-DAB) (3) seems to be the most plausible candidate. It could exist in equilibrium with the mononuclear complex 1, eq 10,

$$2Cr(CO)_5(\text{iprop-DAB}) \rightleftharpoons$$
$$1$$
$$[Cr(CO)_5]_2(\mu\text{-iprop-DAB}) + \text{iprop-DAB} (10)$$
$$3$$
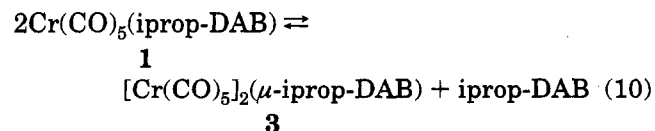
whereby the ratio of the two complexes should depend on the concentration of the free iprop-DAB ligand. Indeed, in support of this consideration the intensity of

(20) A similar spectrum of 1 and analogous spectral changes occurring at ambient temperature are observed in toluene-d_8 solution (cf. Table 2).
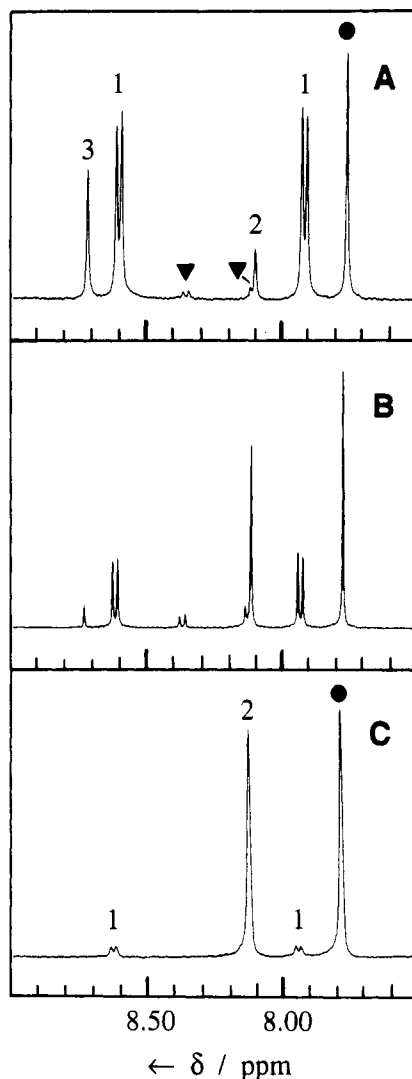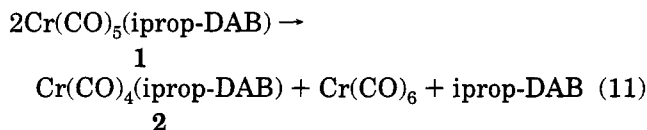

Figure 2. Part of the ^{1}H-NMR spectrum ($=CH-$ region) of $Cr(CO)_5$(iprop-DAB) (1, ca. 75 mM) in $C_6D_{11}CD_3$ recorded (A) shortly after warming to 300 K, (B) after 2 h at 300 K, and (C) after 24 h at 300 K. The particular signals are associated with $Cr(CO)_5$(iprop-DAB) (1), $Cr(CO)_4$(iprop-DAB) (2), $[Cr(CO)_5]_2$(iprop-DAB) (3), free iprop-DAB (●), and an isomeric species of 1 (▼, tentative assignment); cf. Table 2. Note that the individual spectra are normalized to the most intense signal.

the singlet attributed to 3 decreases to nearly the detection level when 1 is dissolved in the presence of a large excess of iprop-DAB (375 mM).

The spectral changes occurring upon standing at 300 K (Figure 2B,C) indicate that complex 1 gradually disappears with concurrent formation of 2 and liberation of iprop-DAB. Worthwhile to note, the gradual increase in the concentration of free iprop-DAB in the course of this process is paralleled by a decrease in the ratio of the di- and mononuclear $Cr(CO)_5$ complexes 3 and 1, as expected on the basis of the equilibrium according to eq 10. The decay of 1 under the conditions of this experiment finally yields the chelate complex 2 and free iprop-DAB in a 1:1 molar ratio (Figure 2C). The ^{13}C-NMR spectrum of the same sample solution reveals that in addition to these two products a substantial amount of $Cr(CO)_6$ is formed. For quantitative analysis, the solution was diluted and an IR spectrum was recorded, which showed that equimolar amounts of $Cr(CO)_6$,

chelate complex 2, and free iprop-DAB ligand are formed, eq 11.

$$2Cr(CO)_5(iprop\text{-}DAB) \rightarrow$$
$$\mathbf{1}$$
$$Cr(CO)_4(iprop\text{-}DAB) + Cr(CO)_6 + iprop\text{-}DAB \quad (11)$$
$$\mathbf{2}$$

With this stoichiometry in mind one might suspect that the reaction proceeds via the dinuclear complex [Cr(CO)$_5$]$_2$(μ-iprop-DAB) (3) in such a way that one CO group is directly transferred from one metal atom to the other. However, the formation of Cr(CO)$_6$ as a side product is drastically reduced when the reaction is performed in a wide Schlenck tube, instead of the sealed NMR tube. Conducted in this way, the decay of 1 (75 mM solution in n-hexane) at ambient temperature yields the chelate complex 2 and Cr(CO)$_6$ in a ca. 3:1 molar ratio (with satisfactory material balance), as determined by quantitative IR spectroscopy after 24 h. This result clearly disproves the suspicion of an intramolecular CO transfer involving the dinuclear complex 3. It rather suggests the occurrence of two separate reactions, viz., chelate ring closure of 1 to form 2 with extrusion of CO, which then may displace the iprop-DAB ligand from a second molecule of 1 to form Cr(CO)$_6$. While the liberated CO cannot escape from the sealed NMR tube, some of it may be lost in the Schlenck tube experiment, such that less Cr(CO)$_6$ is formed.

The formation of Cr(CO)$_6$ is greatly enhanced when the decay of 1 occurs in more dilute solutions (1–2 mM in n-hexane). Under such conditions it exceeds the chelate ring closure reaction by a factor of 2.5–4, unless an excess of added free iprop-DAB is present. At the same time the material balance shows a deficit on the order of 20–40%, as determined by quantitative IR spectroscopy. It is clear from these observations that in the absence of added iprop-DAB a substantial amount of Cr(CO)$_5$(iprop-DAB) (1) decomposes with formation of additional Cr(CO)$_6$ and unidentified CO-loss product-(s). Nevertheless, when monitoring the decay of 1 under such conditions at ambient temperature, we note that, despite the intricate stoichiometry of the overall process, it disappears by first-order kinetics. The plot of ln [1] vs time gives a straight line over 2–3 half-lives, the slope of which yields $k_{obs} = 11 \times 10^{-5}$ s^{-1} (Table 1). These data compare well with previous results[6,11] obtained by means of quantitative UV–vis spectroscopy with in situ photogenerated 1. However, this agreement should not be overemphasized since we must not fail to note that in those studies an excess of free DAB ligand was present and, moreover, the re-formation of Cr(CO)$_6$ was not considered as a possible side reaction.
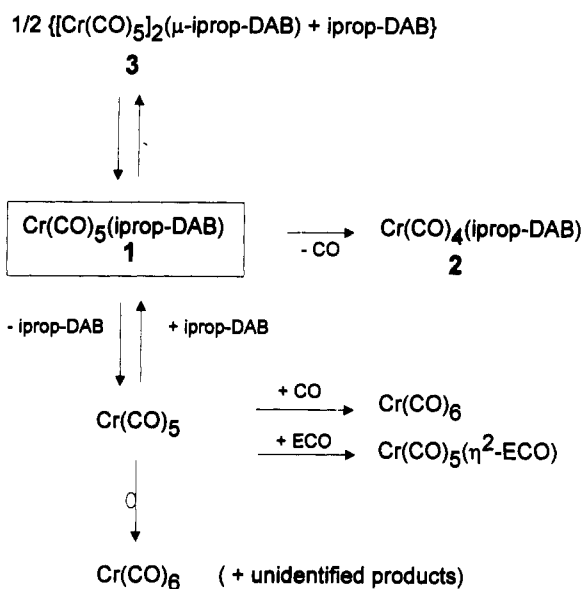
The decay of Cr(CO)$_5$(iprop-DAB) (1) is slowed down in the presence of added iprop-DAB, which also improves the material balance and affects the product ratio in favor of the chelate complex 2. Thus, with a 2-fold excess of iprop-DAB (Table 1, experiment 2) the rate constant is reduced to $k_{obs} = 6.4 \times 10^{-5}$ s^{-1}. This goes along with a discrimination of Cr(CO)$_6$ formation against chelate ring closure such that the two products are formed in nearly a 1:1 molar ratio. A further increase in the concentration of added iprop-DAB (Table 1, experiments 3–6) ultimately leads to a lower limiting value of $k_{obs} = 2.7 \times 10^{-5}$ s^{-1}. At the same time the deficit in the material balance is reduced to less than

Table 1. Decay of Cr(CO)$_5$(N−N) (1) in n-Hexane Solution with Formation of the Cr(CO)$_4$(N−N) Chelate Complex 2 and Cr(CO)$_6$ (N−N = iprop-DAB)

expt	Cr(CO)$_5$(N−N) (1) initial conc. (mM)	Cr(CO)$_5$(N−N) (1) conversion (%)	added N−N (mM)	yield (%)[c] Cr(CO)$_6$	yield (%)[c] Cr(CO)$_4$-(N−N)(2)	10^5k_{obs}[a,b] (s^{-1})
1	1.58	88.6		39.7	10.7	11.0
2	1.20	74.2	2.40	26.6	29.0	6.4
3	1.49	73.3	5.95	23.1	34.1	4.3
4	1.81	75.0	18.5	14.7	55.3	3.1
5	1.17	73.9	23.4	3.9	62.2	2.9
6	1.33	74.8	67	3.3	63.1	2.7
7[d]	0.82	87.6	41	54.0	30.8	8.7
8[e]	1.97	88.9	20	(67.5)[f]	17.4	20.2
9	0.81	75.6	40	2.1	68.9	6.2 (32 °C)
10	1.23	76.2	61.5	3.7	66.1	9.5 (40 °C)
11	0.97	77.2	48.6	3.5	68.8	13.5 (48 °C)

[a] Disappearance of 1. [b] At 23 °C, unless noted otherwise. [c] Based on the initial concentration of 1. [d] Under CO atmosphere, [CO] $\sim$ 10 mM.[24] [e] In the presence of added (E)-cyclooctene (ECO), [ECO] = 19.7 mM. [f] Cr(CO)$_5$(η^2-ECO)[17] is formed instead of Cr(CO)$_6$.

Scheme 1

1/2 {[Cr(CO)$_5$]$_2$(μ-iprop-DAB) + iprop-DAB}
3

Cr(CO)$_5$(iprop-DAB) **1** $\xrightarrow{- CO}$ Cr(CO)$_4$(iprop-DAB) **2**

$- iprop\text{-}DAB$ ↕ $+ iprop\text{-}DAB$

Cr(CO)$_5$ $\xrightarrow{+ CO}$ Cr(CO)$_6$

$\xrightarrow{+ ECO}$ Cr(CO)$_5$(η^2-ECO)

Cr(CO)$_6$ (+ unidentified products)

10% and the formation of Cr(CO)$_6$ is minimized to such an extent that the chelate ring closure predominates by a factor of 20.

These results are consistent with Scheme 1, the key features of which resemble those of the previously investigated dmbpy/Cr(CO)$_5$ system.[18] Complex 1 exists in an equilibrium with the dinuclear species 3. Chelate ring closure with loss of CO and formation of 2 occurs in competition with reversible iprop-DAB dissociation from 1, followed by capturing of the Cr(CO)$_5$ fragment by the liberated CO. The latter dissociative route will be disfavored at a higher concentration of 1 and will be strongly suppressed in the presence of added iprop-DAB, which reduces the steady state concentration of the Cr(CO)$_5$ fragment. This leads to the decrease in the overall decay rate of 1 and to the reduced formation of Cr(CO)$_6$ in the series of experiments 1–6 in Table 1.

The presence of added CO or another potential ligand has the expected counteracting effect. Thus, under a CO atmosphere ([CO] ca. 10^{-2} M) the decay of 1 (Table 1, experiment 7) is accelerated by a factor of 3 ($k_{obs} = 8.7 \times 10^{-5}$ s^{-1}), compared with the data obtained under an argon atmosphere in the presence of similar concen-

trations of added iprop-DAB (Table 1, experiments 5 and 6). The formation of $Cr(CO)_6$ is favored at the expense of chelate ring closure, and the material balance is quantitative within experimental error. The use of (E)-cyclooctene ([ECO] = 19.7 mM), instead of added CO, in a complementary experiment (Table 1, experiment 8) shows that the $Cr(CO)_5$ fragment is likewise efficiently captured. In this case $Cr(CO)_5(\eta^2\text{-ECO})$[17] is formed, while the $Cr(CO)_6$ production remains below the detection level. The plot of ln [1] vs time gives a straight line over 4 half-lives, from which the first-order rate constant k_{obs} = 20.2 × 10^{-5} s^{-1} is determined. This larger value reflects the higher concentration of the trapping agent, ca. 20 mM ECO vs 10 mM CO in a CO-saturated solution. The formation of the chelate complex **2** is accordingly reduced and plays only a minor role. A more detailed kinetic study, aiming at the evaluation of the rate constants associated with the individual processes in Scheme 1 on the basis of experiments with varying concentrations of added iprop-DAB, CO, or other potential ligands, is currently underway, but is beyond the scope of this paper.

Variable-temperature measurements (Table 1, experiments 9—11) were performed under argon atmosphere in the presence of added iprop-DAB in concentrations similar to those in experiment 6. The side reaction leading to $Cr(CO)_6$ remains minimal throughout the whole series, such that the rate constants, to a good approximation, represent the chelate ring closure process. This should also be true for the activation parameters evaluated from an Eyring plot on the basis of these data, which yields $\Delta H^{\ddagger}$ = 48 ± 6 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −170 ± 18 J mol^{-1} K^{-1}.

The large negative value of the activation entropy is in accord with the assumption of some associative character in the transition state of this intramolecular CO substitution.[6] In contrast to this interpretation the activation volume of the process was previously found to be significantly positive, as determined from variable-pressure kinetic measurements using in situ photogenerated monodentate complex **1**.[11] This led to the conclusion that the chelate ring closure proceeds via the dissociation of CO.[11] However, one has to keep in mind that in this previous study added iprop-DAB was present only in a 5 mM concentration and that the photodissociated CO apparently was not removed from the solution. Hence it seems possible that under such conditions the side reaction leading to $Cr(CO)_6$ was not kept at a negligibly low level. If so, the activation parameters determined from those experiments would not be characteristic of the chelate ring closure alone, but to some extent they might also reflect the displacement of the iprop-DAB ligand by CO, which most likely involves a dissociative transition state.

For comparison with the IR spectroscopic results the decay of **1** (ca. 0.3 mM in n-hexane solution) in the presence of a 10-fold excess of iprop-DAB was also monitored by quantitative UV—vis spectroscopy. The spectra displayed in Figure 3 show the course of the reaction over slightly less than 2 half-lives. The decay of the maximum at λ = 405 nm represents the gradual disappearance of the monodentate complex **1**, while the absorption of the chelate complex **2** concurrently appears at λ_{max} = 586 nm. The reaction proceeds by first-order kinetics, and the evaluation of the rate constant
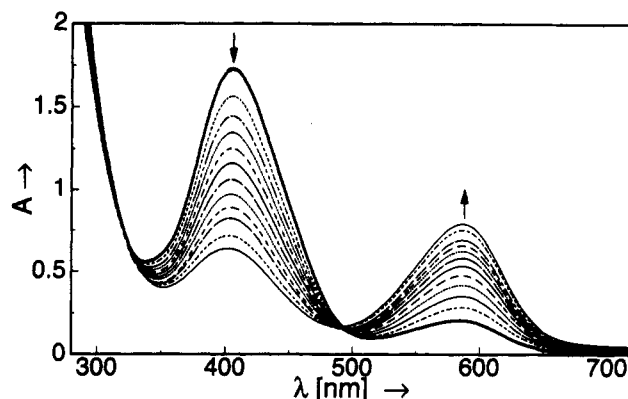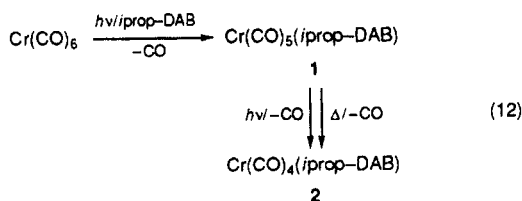

Figure 3. UV—vis spectrum of $Cr(CO)_5(\text{iprop-DAB})$ (**1**, 0.3 mM; bold line, λ_{max} = 405 nm) in n-hexane in the presence of added iprop-DAB (3 mM) at ambient temperature. Subsequently occurring spectral changes (recorded after 30, 60, 90, 120, 150, 180, 210, 240, 270, 330, and 390 min) indicate the formation of the $Cr(CO)_4(\text{iprop-DAB})$ chelate complex (**2**; λ_{max} = 586 nm); note the isosbestic point near 490 nm.

from a plot of $\ln[(A_\infty - A_t)/(A_\infty - A_0)]$ vs time yields k_{obs} = 4.2 × 10^{-5} s^{-1} for the appearance of $Cr(CO)_4(\text{iprop-DAB})$ (**2**) and k_{obs} = 5.1 × 10^{-5} s^{-1} for the disappearance of $Cr(CO)_5(\text{iprop-DAB})$ (**1**). These data compare well with those obtained by quantitative IR spectroscopy at similar concentrations of added iprop-DAB (Table 1, experiments 2 and 3). Moreover, on the basis of the quantitative UV—vis absorbance data of the two compounds (see Experimental Section) we recognize that actually no more than 30—35% of **1** is converted into **2**, which is also in accord with the stoichiometry determined by means of quantitative IR spectroscopy. Clearly, the observation of an isosbestic point (Figure 3) cannot be taken as a criterion for the conversion of the starting material into one single product; it just indicates that products are formed in a (nearly) constant ratio throughout the course of the reaction.

As a final point deserving some attention we wish to expand on the actual relevance of the *thermal* chelate ring closure of **1** to the overall process of the photochemical conversion of $Cr(CO)_6$ into the $Cr(CO)_4(\text{iprop-DAB})$ chelate complex **2**, eq 8. Clearly, the monodentate complex $Cr(CO)_5(\text{iprop-DAB})$ (**1**) emerges as an intermediate product, but we note that under continuous irradiation the formation of **2**, in general, is terminated much faster than expected on the basis of the thermal ring closure rate constant. Thus, in a typical run on a preparative scale the conversion of $Cr(CO)_6$ (7 mM in n-hexane, 350-mL solution) into **2** upon irradiation with a Philips HPK 125-W lamp through solidex glass in the presence of excess iprop-DAB (10.7 mM) is brought to completion after ca. 3 h. At this time no more than ca. 35% of intermediately formed **1** could have decayed thermally. Even at −20 °C, where the lifetime of **1** in the dark exceeds 1 or 2 days, the chelate complex **2** is likewise rapidly formed when a solution of $Cr(CO)_6$ (6 mM) and iprop-DAB (12 mM) is continuously irradiated as described above, while the monodentate intermediate product **1** does not accumulate to a sizable concentration. Similar observations were made in complementary analytical scale studies with lower concentrations of $Cr(CO)_6$ (ca. 0.3 mM) employing both IR and UV—vis spectroscopy for monitoring the course of the conversion.

These findings indicate that under continuous ir-

radiation photogenerated Cr(CO)$_5$(iprop-DAB) (**1**) subsequently undergoes *photolytic* CO loss and chelate ring closure as a rather efficient process. In other words, in practice the photochemical synthesis of Cr(CO)$_4$(iprop-DAB) (**2**) essentially involves two consecutive photolytic steps, eq 12, with a possible minor contribution of

$$Cr(CO)_6 \xrightarrow[-CO]{h\nu/iprop\text{-}DAB} Cr(CO)_5(iprop\text{-}DAB) \qquad (12)$$
$$\mathbf{1}$$
$$h\nu/-CO \updownarrow \Delta/-CO$$
$$Cr(CO)_4(iprop\text{-}DAB)$$
$$\mathbf{2}$$

thermal chelate ring closure of the intermediate product **1**. Clearly, this latter process becomes more relevant at longer reaction times, i.e., in experiments with low intensity irradiation or high initial concentration of Cr-(CO)$_6$.

The spectral composition of the incident light is an important factor in this context. Comparing the above broad-band irradiation with short-wavelength monochromatic photolysis ($\lambda = 302$ nm) of Cr(CO)$_6$ (ca. 0.3 mM in *n*-hexane) and excess iprop-DAB, we note that in the latter case the appearance of the chelate product **2** is considerably retarded, while the monodentate species **1** intermediately accumulates to a level of ca. 40% of the total complex concentration. This wavelength-dependent behavior of the system reflects the large differences in the UV−vis spectra of Cr(CO)$_6$ on the one hand and the substituted complexes **1** and **2** on the other hand. The parent hexacarbonyl is a colorless complex and thus exerts no significant internal light filter effect at longer wavelengths. Therefore, already at a low concentration of **1** this deeply colored compound ($\lambda_{max} = 405$ nm) is able to absorb light from a polychromatic light source and thus readily undergoes photolytic CO dissociation with chelate ring closure. As a consequence of this, the in situ photogeneration of the monodentate species **1** should preferably be performed by using short-wavelength irradiation. Moreover, it is clear from these exploratory studies that reliable and meaningful quantum yield data can only be obtained with correct consideration of internal light filtering.

Conclusion

The decay of Cr(CO)$_5$(iprop-DAB) (**1**) (Scheme 1) in some respect resembles the behavior of the related dmbpy/Cr(CO)$_5$ system,[18] since in both cases the intramolecular chelate ring closure occurs in competition with loss of the N−N ligand and Cr(CO)$_6$ formation. However, there is a marked difference concerning the influence of added free ligand on the kinetics. This is due to the fact that the dmbpy/Cr(CO)$_5$ system involves the dinuclear [Cr(CO)$_5$]$_2$(μ-dmbpy) complex as the starting material, which first takes up free dmbpy to form the mononuclear Cr(CO)$_5$(dmbpy) species, eqs 4 and 5. As a consequence of this, the decay with ultimate formation of Cr(CO)$_6$ and Cr(CO)$_4$(dmbpy), eqs 6 and 7, is greatly accelerated upon addition of excess free ligand. By contrast, the related equilibrium between [Cr(CO)$_5$]$_2$-(μ-iprop-DAB) (**3**) and Cr(CO)$_5$(iprop-DAB) (**1**), eq 10, involves only a minor amount of the dinuclear species, such that the addition of free iprop-DAB mainly affects

the reversible loss of the ligand from Cr(CO)$_5$(iprop-DAB) (**1**), Scheme 1. This way the formation of Cr(CO)$_6$ via the Cr(CO)$_5$ fragment is largely suppressed and the overall decay of **1** is retarded.

In conclusion this study has demonstrated that caution has to be exercised in drawing conclusions by analogy, solely on the basis of UV−vis and/or IR spectral information and kinetic data, even in cases of apparently closely related systems. Reliable information on the material balance and comprehensive characterization of the relevant species is highly desirable, if not indispensible, for achieving a deeper understanding of the events occurring in such multistep reactions.

Experimental Section

Materials and Equipment. Syntheses and manipulations of the organometallic compounds were performed in deoxygenated solvents under an inert (argon) atmosphere using standard Schlenk techniques throughout. Analytical grade and deuterated solvents, (*Z*)-cyclooctene, and hexacarbonyl-chromium were purchased from Merck (Darmstadt). Penta-carbonyl(η^2-(*Z*)-cyclooctene)chromium,[17] 1,4-diisopropyl-1,4-diazabutadiene,[6] and (*E*)-cyclooctene[21] were prepared according to the published procedures.

Spectra were recorded using the following instruments: IR Perkin-Elmer 881, operating with slit program 3/filter 4; UV−vis Omega 10, Bruins Instruments (Puchheim); NMR Bruker AM 400 and Bruker AC 270. Melting points were determined in evacuated and sealed capillaries using a Büchi/Tottoli apparatus. Elemental analysis was by Mikroanalytisches Laboratorium Dornis und Kolbe, Mülheim an der Ruhr.

Pentacarbonyl(1,4-diisopropyl-1,4-diazabutadiene)-chromium (1). Pentacarbonyl((*Z*)-cyclooctene)chromium (0.90 g, 3.0 mmol) is dissolved in a precooled solution (−50 °C) of 1,4-diisopropyl-1,4-diazabutadiene (0.84 g, 6.0 mmol) in *n*-hexane (200 mL). The solution is continuously stirred and warmed to ambient temperature, whereupon the color changes from pale yellow to deep orange-red. After 15 min the solution is immediately cooled and kept at dry-ice temperature for 3 days. Red crystals of **1** precipitate, which are separated from the supernatant solution by inverse filtration and dried in vacuo; yield 0.67 g (67%), mp 45 °C. Anal. Calcd for C$_{13}$H$_{16}$CrN$_2$O$_5$: C, 46.99; H, 4.85; Cr, 15.65; N, 8.43. Found: C, 46.19; H, 4.65; Cr, 16.06; N, 8.70. IR (*n*-hexane): $\tilde{\nu}_{CO}$ (ϵ) = 2067 (1240), 1940 (13 220), and 1925 cm^{-1} (7220 L mol^{-1} cm^{-1}). UV−vis (*n*-hexane): λ_{max} (ϵ) = 248 (24 900) and 405 nm (4450 L mol^{-1} cm^{-1}); a weak absorption near 560 nm is possibly due to the formation of a trace amount of Cr(CO)$_4$(iprop-DAB) (**2**); cf. lit. data for **1** (λ_{max} 402 nm, in benzene).[6] ^{1}H-NMR data are listed in Table 2. ^{13}C{^{1}H}-NMR (toluene-*d$_8$*, 100.6 MHz, 253 K): δ 23.48/21.86 (−CH*Me$_2$*), 68.96/62.86 (−C*H*Me$_2$), 169.91/157.62 (=C*H*−), 214.58 (eq-*C*O), 220.89 (ax-*C*O); additional, weak signals are attributable to **2**, **3**, iprop-DAB, and the **1** isomer species. NMR data for 1,4-diisopropyl-1,4-diazabutadiene (authentic sample): ^{1}H-NMR (methylcyclo-hexane-*d$_{14}$*, 400.1 MHz, 300 K) δ 7.79 (=C*H*−), 3.37 and 1.15 (−C*H*Me$_2$ and −CH*Me$_2$*, ^3J = 6.2 Hz); ^{13}C{^{1}H}-NMR (methyl-cyclohexane-*d$_{14}$*, 100.6 MHz, 300 K) δ 24.11 (−CH*Me$_2$*), 61.88 (−C*H*Me$_2$), 159.45 (=C*H*−).

Tetracarbonyl(1,4-diisopropyl-1,4-diazabutadiene)-chromium (2). A solution of hexacarbonylchromium (0.55 g, 2.5 mmol) and 1,4-diisopropyl-1,4-diazabutadiene (0.52 g, 3.7 mmol) in *n*-hexane (350 mL) is placed in an immersion-well photochemical reaction vessel[22] (solidex glass, $\lambda \geq 280$ nm) and

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Table 2. ^{1}H-NMR Data [δ/ppm (multiplicity, J/Hz)] of Cr(CO)$_5$(iprop-DAB) (1) and Related Species Present in the Sample Solution

cpd	=CH−	−CHMe$_2$	−CHMe$_2$
	(a) Spectrum Recorded in Toluene-d_8 at 250 K		
1[a]	8.56 (d, 7.4), 7.60 (d, 7.4)	3.57 (sept, 6.6), 3.25 (sept, 6.2)	1.04 (d, 6.2), 0.38 (d, 6.6)
2	6.60	(?)	1.17 (d)
3	8.35	(?)	0.73 (d)
iprop-DAB	7.83	3.03 (sept)	(?)
1 isomer	8.33 (d), 7.34 (d)	(?), (?)	0.94 (d), 0.80 (d)
	(b) Spectrum Recorded in Toluene-d_8 at 298 K		
1	8.55 (d, 7.4), 7.64 (d, 7.4)	3.70 (sept, 6.6), 3.36 (sept, 6.2)	1.04 (d, 6.2), 0.54 (d, 6.6)
2	6.93	3.72 (sept, ~6.5)	1.18 (d, 6.5)
3	8.39	3.82 (sept, 6.6)	0.84 (d, 6.6)
iprop-DAB	7.79	3.10 (sept, 6.4)	1.02 (d, 6.4)
1 isomer	8.31 (d, 8.3), 7.48 (d, 8.3)	3.12 (sept), 2.98 (sept, 6.3)	0.93 (d, 6.3), 0.89 (d, 6.6)
	(c) Spectrum Recorded in Methylcyclohexane-d_{14} at 300 K (cf. Figure 2A)[b]		
1	8.63 (d, 7.4), 7.94 (d, 7.4)	4.23 (sept, 6.6), 3.66 (sept, 6.2)	(?), (?)
2	8.13	4.40 (sept, 6.6)	(?)
3	8.74	4.36 (sept, 6.6)	(?)
iprop-DAB	7.79	3.37 (sept, 6.2)	(?)
1 isomer	8.38 (d), 8.14 (d)	3.43 (sept) (?)	(?), (?)

[a] Signals associated with 1 account for ca. 85% of the total intensity. [b] −CHMe$_2$ data overlap with solvent signals.

irradiated (Philips HPK 125-W lamp) for 3 h at ambient temperature. Removal of the solvent in vacuo followed by recrystallization of the residue from *n*-hexane (ca. 15 mL) at dry-ice temperature yields violet crystals of 2; yield 0.54 g (71%), mp 123 °C. IR (*n*-hexane): $\bar{\nu}_{CO}$ (ϵ) = 2015 (3500), 1925 (12 590), ~1920 (sh), and 1871 cm^{-1} (5950 L mol^{-1} cm^{-1}); cf. lit. data [2013.6 (a_1), 1924.6 (b_1), 1917.2 (a_1), and 1869.7 (b_2) cm^{-1}].[23] UV−vis (*n*-hexane): λ_{max} (ϵ) = 383 (1380) and 586 nm (8140 L mol^{-1} cm^{-1}); cf. lit. data [λ_{max} 389 nm (d → d) and 562 nm (MLCT), in benzene].[6] ^{1}H-NMR (toluene-d_8, 400.1 MHz, 300 K): δ 6.92 (=CH−), 3.73 and 1.18 (−CHMe$_2$ and −CHMe_2, ^3J = 6.5 Hz); cf. data collected in Table 2. ^{13}C{^{1}H}-NMR (toluene-d_8, 100.6 MHz, 300 K): δ 23.94 (−CHMe_2), 65.75 (−CHMe$_2$), 155.14 (=CH−), 213.18 (CO), and 231.48 (CO).

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Decay Kinetics of Cr(CO)$_5$(iprop-DAB) (1) Monitored by Means of IR Spectroscopy. Solutions (50 mL) of complex 1 (1−2 mM, see Table 1) and added iprop-DAB (and (*E*)-cyclooctene, experiment 8) in *n*-hexane were placed in a thermostated reaction vessel, wrapped with aluminum foil, and stirred under an argon (or CO, experiment 7) atmosphere at the appropriate temperature. Samples were drawn every 30 min over 2−3 half-lives and analyzed by means of quantitative IR spectroscopy (IR cell with CaF$_2$ windows, d = 494 μm) on the basis of the ν_{CO} data for 1 (ϵ = 13 220 L mol^{-1} cm^{-1} at 1940 cm^{-1}), 2 (ϵ = 5950 L mol^{-1} cm^{-1} at 1871 cm^{-1}), Cr(CO)$_6$ (ϵ = 33 400 L mol^{-1} cm^{-1} at 1989 cm^{-1}), and Cr(CO)$_5$(η^2-ECO)[17] (ϵ = 18 700 L mol^{-1} cm^{-1} at 1960 cm^{-1}). Rate constants evaluated from plots of ln [1] vs time are listed in Table 1 together with the total conversions of 1 and the ultimately observed yields of 2 and Cr(CO)$_6$.