

## CO-induced, reversible insertion of a terminal imido ligand into an $\eta^1:\eta^2$ -isocyanide bridge in the dimolybdenum complex $\text{Cp}(\text{CO})_2\text{Mo}(\mu\text{-CNPh})\text{Mo}(\text{NPh})\text{Cp}$ ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ )

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### Abstract

High pressure carbonylation of  $\text{Cp}(\text{CO})_2\text{Mo}(\text{CNPh})\text{Mo}(\text{NPh})\text{Cp}$  (*Mo–Mo*) gives a product that has been shown by an X-ray diffraction study to be a metalla-amidinato complex. This means that the originally present terminal phenylimido ligand inserts into an  $\eta^2$ , ( $\sigma + \pi$ )-bonded isocyanide bridge to form a four-membered heterocycle in which a  $\text{Cp}(\text{CO})_2\text{Mo}$  unit is coordinated by both N atoms, whereas a  $\text{Cp}(\text{CO})_3\text{Mo}$  unit is attached to the central carbon atom. In boiling toluene this process is reversed, with release of CO. A by-product in this reaction is a mononuclear  $\text{Cp}(\text{CO})_2\text{Mo}$ -amidinato complex bearing a cyclopentadiene group at the central C atom.

### Introduction

Numerous examples of activation of heteroallenes by transition-metal complexes have been described [1]. However, the addition of such unsaturated molecules to complexes containing metal–metal multiple bonds, e.g.  $[\eta^5\text{-C}_5\text{R}_5\text{M}(\text{CO})_2]_2$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ;  $\text{R} = \text{H}, \text{CH}_3$ ) [2], has been investigated in relatively few cases [3]. Recently we described the cleavage of diphenylcarbodiimide by  $[\text{CpMo}(\text{CO})_2]_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) into a phenylimido and an isocyanide ligand [4]. The resulting complex  $\text{Cp}(\text{CO})_2\text{Mo}(\mu, \eta^2\text{-CNPh})\text{Mo}(\text{NPh})\text{Cp}$  (I) undergoes two reactions that are surprising in view of the generally accepted stability of the M–N bond in organoimido complexes [5]. Thus, I undergoes a substitution reaction with an excess of  $\text{P}(\text{OMe})_3$  to form a compound in which the terminal imido ligand is replaced by an oxo ligand [4], and it consumes three molecules of CO in a high pressure reaction (250 bar) [6].

On the basis of preliminary spectroscopic data obtained for the product of the latter reaction a dinuclear structure containing a non-bridging  $\eta^2$ -PhN=C=NPh ligand was proposed [6]. In this paper we describe the results of an X-ray investigation of complex II, which confirm that I has incorporated three CO molecules, but that as a consequence of CO addition a completely new metalla-amidinato skeleton has been formed. Upon thermolysis of II, I is reformed along with a second complex, III, which has been shown from its spectroscopic data to be a mononuclear amidinato complex, bearing a  $C_5H_5$ -group at the amidinato-C-atom.

## Experimental

**General data.** All procedures were carried out under nitrogen with anhydrous  $N_2$ -saturated solvents. Elemental analyses were performed by the Mikroanalytisches Laboratorium, Universität Regensburg. IR spectra were obtained with a Beckman 4240 spectrophotometer. Field desorption mass spectra were determined with a Varian 311A instrument. NMR spectra were recorded on a Bruker WM250 instrument.  $Cp_2(CO)_2Mo_2(CNPh)(NPh)$  (I) was prepared as described previously from  $[CpMo(CO)_2]_2$  and a tenfold excess of  $PhN=C=NPh$  in toluene at  $100^\circ C$  [6].

### Preparations

**Reaction of I with CO.** A solution of I (400 mg, 0.7 mmol) in 20 ml of toluene was placed in a 100 ml autoclave. After three purges with 50 atm of CO, the solution was stirred under 250 atm of CO for 20 h at  $40^\circ C$ . The mixture was chromatographed on  $SiO_2$  (column  $22 \times 4$  cm). Elution with toluene gave 124 mg (27%) of the orange-red complex II, which gave red-brown prisms upon recrystallization from ether/pentane 1/1. Anal. Found: C, 51.17; H, 3.11; N, 4.25; O, 11.77; mol wt 648 (field desorption MS related to  $^{92}Mo$ , from toluene solution).  $C_{28}H_{20}Mo_2N_2O_5$  (II) calcd.: C, 51.24; H, 3.07; N, 4.27; O, 12.19%; mol wt 656.4. II: m.p.  $157^\circ C$  (dec); IR (KBr)  $\nu(CO)$  2017(m), 1952(s), 1928(s), 1843(s),  $\nu(N-C-N)$

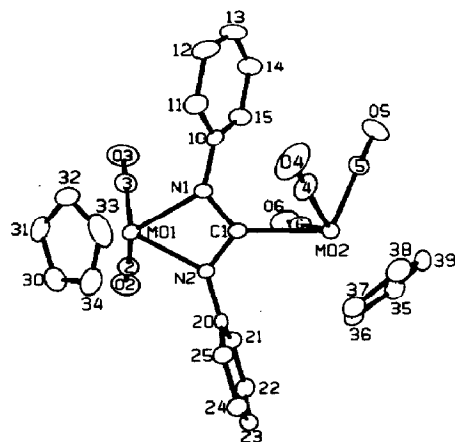


Fig. 1. ORTEP drawing of the molecular structure of II.

1592(m), 1492(m), 1391(s)  $\text{cm}^{-1}$ ;  $^1\text{H NMR } \delta(\text{C}_5\text{H}_5)$  4.80(s), 5.35(s),  $\delta(\text{C}_6\text{H}_5)$  7.09–7.30(m) ( $\text{CDCl}_3$ ).

**Thermolysis of II.** A solution of 370 mg (0.56 mmol) of II in 100 ml of toluene was refluxed for 2.5 h. Chromatography on  $\text{SiO}_2$  (column  $30 \times 4$  cm) of the concentrated solution gave successively 61 mg (22%) of orange III and 219 mg (68%) of a dark red complex, both eluted with toluene. The latter was shown to be identical with I by means of IR and  $^1\text{H NMR}$  spectroscopy [4]. Recrystallization of III from ether/pentane 2/1 gave orange-red crystals. Anal. Found: C, 63.41; H, 3.50; mol wt 472 (field desorption MS related to  $^{92}\text{Mo}$ , from toluene solution).  $\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_2\text{Mo}$  (III) calcd.: C, 63.03; H, 4.23%; mol wt 476.4. III: m.p.  $176^\circ\text{C}$  (dec); IR (KBr)  $\nu(\text{CO})$  1952(vs), 1858(vs),  $\nu(\text{N}-\text{C}-\text{N})$  1593(m) 1494(m), 1430(s)  $\text{cm}^{-1}$ ;  $^1\text{H NMR } \delta(\text{C}_5\text{H}_5)$  5.56(s), 5.58(s),  $\delta(\text{C}_5\text{H}_5\text{R})$  2.66(m), 2.85, 5.98(m), 6.24(m),  $\delta(\text{C}_6\text{H}_5)$  6.84(m), 6.97(m), 7.20(m) ( $\text{CDCl}_3$ ).

**Structure solution of I.** An Enraf–Nonius CAD4 automatic diffractometer was used, with  $\text{Mo-K}_\alpha$  radiation monochromatized by a dense graphite crystal assumed to be ideally imperfect. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table 1.

From the Niggli matrix and systematic absences the space group was found to be  $P2_1/c$  (No. 14). Intensities were measured by the  $\theta$ – $2\theta$  scan technique, with the scan rate depending on the net count obtained in rapid pre-scans of each reflection. An empirical absorption correction was applied.

The structure was solved by use of SIMPEL 82 [7], which revealed the positions of the molybdenum atoms. All other non-hydrogen atoms were located in subsequent difference Fourier syntheses. The hydrogen atoms were calculated at ideal positions and not refined.

Table 1  
Crystallographic Data

	$\text{Mo}_2\text{C}_{28}\text{H}_{20}\text{O}_5\text{N}_2$ (II)
mol wt, g/mol	656.36
crystal size, mm	$0.32 \times 0.29 \times 0.37$
cell const $a$ , Å	19.444(4)
$b$ , Å	8.116(1)
$c$ , Å	17.059(2)
$\beta$ , deg	105.07(1)
cell vol, Å <sup>3</sup>	2299.4
$Z$	4
$d$ (calcd), g/cm <sup>3</sup>	1.608
abs coeff, $\text{cm}^{-1}$	9.7
data collection range	$2^\circ \leq \theta \leq 20^\circ$
scan width	$\Delta\theta = (0.9 + 0.35 \tan \theta)$
max scan time, s	120
total data collected	2727
data with $I > 3(I)$	1944
total variables	344
$R = \sum   F_0  -  F_c  / \sum  F_0 $	0.021
$R_w = [\sum w( F_0  -  F_c )^2 / \sum w  F_0 ^2]^{1/2}$	0.021

Table 2

Positional parameters and equivalent isotropic thermal parameters of II (Estimated standard deviations are given in parentheses) <sup>a</sup>

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
Mo(1)	0.65560(2)	0.65144(5)	0.57006(2)	2.772(9)
Mo(2)	0.83552(2)	0.47589(5)	0.42752(2)	2.88(1)
O(2)	0.5476(2)	0.8532(4)	0.4379(2)	6.3(1)
O(3)	0.6953(2)	1.0184(5)	0.6067(2)	7.6(1)
O(4)	0.8942(2)	0.3421(5)	0.6046(2)	9.1(1)
O(5)	0.9693(2)	0.6984(5)	0.4721(3)	7.7(1)
O(6)	0.7724(2)	0.8262(4)	0.3305(2)	6.0(1)
N(1)	0.7651(2)	0.6316(4)	0.5670(2)	2.92(9)
N(2)	0.6837(2)	0.5304(4)	0.4712(2)	2.60(9)
C(1)	0.7540(2)	0.5509(5)	0.4960(2)	2.5(1)
C(2)	0.5880(2)	0.7774(6)	0.4859(3)	3.9(1)
C(3)	0.6808(2)	0.8797(7)	0.5933(3)	4.7(1)
C(4)	0.8723(3)	0.3930(7)	0.5415(3)	5.0(1)
C(5)	0.9201(2)	0.6150(7)	0.4574(3)	4.7(1)
C(6)	0.7954(2)	0.6974(6)	0.3987(3)	3.7(1)
C(10)	0.8288(2)	0.7025(6)	0.6154(2)	3.2(1)
C(11)	0.8569(3)	0.6410(6)	0.6942(3)	4.5(1)
C(12)	0.9176(3)	0.7113(7)	0.7439(3)	5.9(2)
C(13)	0.9507(3)	0.8387(7)	0.7166(3)	6.4(2)
C(14)	0.9228(3)	0.9019(7)	0.6400(3)	5.7(2)
C(15)	0.3617(2)	0.3342(6)	0.5905(3)	4.4(1)
C(20)	0.6445(2)	0.4438(5)	0.4019(2)	2.6(1)
C(21)	0.6130(2)	0.5280(6)	0.3306(2)	3.3(1)
C(22)	0.5737(2)	0.4420(6)	0.2638(2)	4.0(1)
C(23)	0.5645(2)	0.2769(6)	0.2671(3)	4.0(1)
C(24)	0.5939(3)	0.1942(6)	0.3380(3)	4.2(1)
C(25)	0.6338(2)	0.2754(6)	0.4057(2)	3.2(1)
C(30)	0.5620(2)	0.5199(7)	0.6082(3)	4.8(1)
C(31)	0.5944(3)	0.6265(7)	0.6678(3)	5.7(1)
C(32)	0.6638(3)	0.5703(9)	0.7011(3)	7.1(2)
C(33)	0.6708(3)	0.4271(7)	0.6536(3)	6.4(2)
C(34)	0.6081(3)	0.3987(7)	0.6035(3)	5.7(1)
C(35)	0.3262(3)	0.4040(7)	0.2924(3)	5.0(1)
C(36)	0.7633(2)	0.3329(6)	0.3144(3)	4.5(1)
C(37)	0.7947(3)	0.2172(6)	0.3747(3)	4.8(1)
C(38)	0.8697(3)	0.2176(7)	0.3897(3)	5.5(1)
C(39)	0.8881(3)	0.3327(7)	0.3384(3)	5.6(1)

<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:  $\frac{4}{3}[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

## Results

*The carbonylation of Cp(CO)<sub>2</sub>Mo(CNPh)Mo(NPh)Cp (I).* As reported previously [6], I adds three molecules of CO under forcing conditions (40 °C, 250 atm CO, eq. 1). To account for this it was originally assumed that CO uptake induces the formation of a side-on coordinated  $\eta^2$ -carbodiimide ligand (see complex II', eq. 1) in order to achieve a closed valence shell for each metal atom. This process would involve the recombination of the originally employed carbodiimide from two

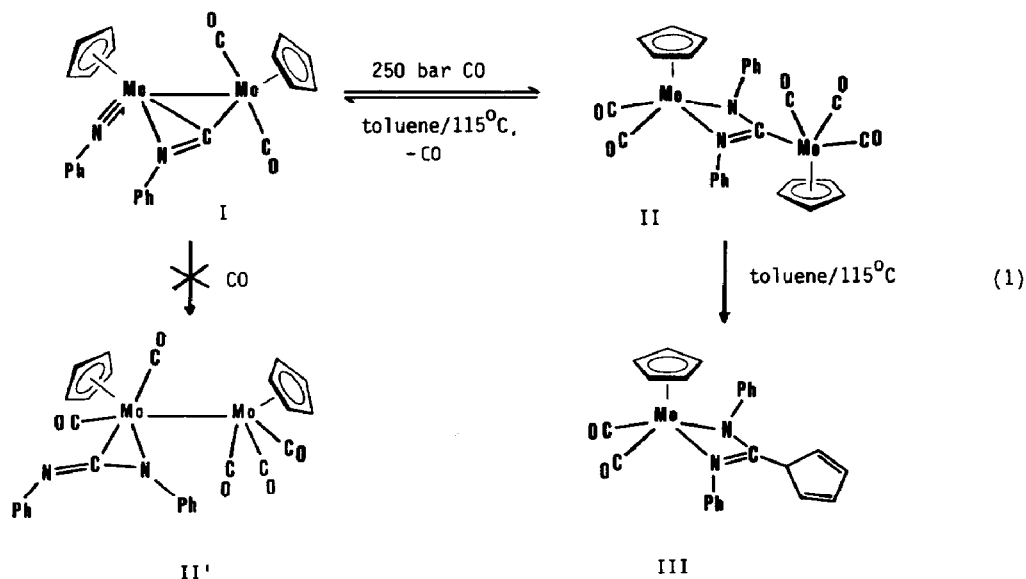
Table 3  
Selected Bond Lengths and Angles for II

Bond Lengths (Å)		Angles (°)	
Mo(1)–N(1)	2.149(2)	N(1)–Mo(1)–N(2)	59.32(9)
Mo(1)–N(2)	2.141(2)	N(1)–Mo(1)–C(3)	82.9(1)
Mo(1)–C(2)	1.963(4)	N(2)–Mo(1)–C(3)	119.9(10)
Mo(1)–C(3)	1.931(4)	C(2)–Mo(1)–C(3)	74.7(1)
Mo(2)–C(1)	2.283(3)	C(1)–Mo(2)–C(4)	72.9
Mo(2)–C(4)	1.992(4)	C(1)–Mo(2)–C(5)	111.2(1)
Mo(2)–C(5)	1.950(4)	C(1)–Mo(2)–C(6)	66.5(1)
Mo(2)–C(6)	1.971(4)	Mo(1)–N(1)–C(10)	132.5(2)
N(1)–C(1)	1.344(3)	Mo(1)–N(1)–C(1)	97.5(2)
N(2)–C(1)	1.333(3)	C(1)–N(1)–C(10)	129.2(3)
		Mo(1)–N(2)–C(20)	133.9(2)
N(1)–C(10)	1.420(4)	Mo(1)–N(2)–C(1)	98.2(2)
N(2)–C(20)	1.416(4)	C(1)–N(2)–C(20)	127.7(3)
Mo(1)–Cp(1)(cent)	2.015	Mo(2)–C(1)–N(1)	128.4(2)
Mo(2)–Cp(2)(cent)	2.018	Mo(2)–C(1)–N(2)	126.5(2)
		N(1)–C(1)–N(2)	104.9(3)

independent N and C containing building blocks. The confirmation of the unusual character of the reaction by an X-ray diffraction study was prevented for a long time by an insufficient crystal quality. Finally, suitable single crystals of II were obtained from ether/pentane mixtures by the diffusion method. The atomic parameters, bond lengths, and angles are presented in Tables 2 and 3. An ORTEP drawing of II is shown in Fig. 1.

The structure determination did, indeed, reveal an N–C–N skeleton, but surprisingly as part of a planar four-membered heterocycle additionally comprising Mo(1), to which two CO groups and the C<sub>5</sub>H<sub>5</sub> ligand are attached. The second molybdenum atom of the Mo–Mo bond originally present in I is attached to the central carbon atom as Cp(CO)<sub>3</sub>Mo-fragment. In this metalla-amidinato arrangement (complex II seems to be the first example of a structurally characterized metalla-amidinato complex [8\*]) the ligand serves as a (3 + 1) electron donor, allowing both Mo atoms to achieve an 18e-configuration. The Mo(1)–N bonds (2.149(2) and 2.141(2) Å) are slightly shorter than a molybdenum nitrogen single bond (2.18–2.25 Å) [9]. The lengths of the N–C bonds in the chelate ligand (1.344(3) and 1.333(3) Å) are between those normally found for single bonds (1.48 Å) and double bonds (1.27 Å) [9]. The two nitrogen atoms and C(1) are in a trigonal planar configuration, indicating that the nitrogen lone pair electrons take part in electron delocalization within the four-membered ring. These observations are in good agreement with structurally and electronically related benzamidinato complex [10]. The Mo(2)–C(1) distance of 2.283(3) Å of II is in the usual range for a Mo–C(sp<sup>2</sup>) single bond [11]. Except for the Cp ring at Mo(1), which is slightly tilted, with C(34) farthest away from Mo(1), and the phenyl groups, which are twisted by 69.2° (C(10)–C(15)) and

\* Reference number with asterisk indicates a note in the list of references.



Scheme 1.

87° (C(20)–C(25)) with respect to a plane through N(1), N(2), C(1), the other groups of the molecule do not show any peculiarities.

As a consequence of the X-ray diffraction results the IR spectrum of II had to be reconsidered. Thus, the  $\nu(\text{CO})$  frequency at  $1793\text{ cm}^{-1}$ , characteristic of the semi-bridging CO group in I, has disappeared and four  $\nu(\text{CO})$  frequencies appear in the terminal region, due to the characteristic absorptions of the  $\text{Cp}(\text{CO})_2\text{Mo}$  and the  $\text{Cp}(\text{CO})_3\text{Mo}$  moieties. A change is also observed in the  $\nu(\text{CN})$  region, where the absorptions of the isocyanide ligand of I ( $1602, 1580\text{ cm}^{-1}$ ) are converted into those of the amidinato ligand ( $1592, 1492, 1391\text{ cm}^{-1}$ ). The incorporation of the CO groups gives rise to a considerable increase in shielding of the Cp protons, as shown by the appearance of the  $^1\text{H}$  NMR resonances at 4.80 and 5.35 ppm (II) compared with 5.40 and 5.70 ppm (I). As a further consequence the broad multiplets of the imido and isocyanide aromatic protons of I (6.85–7.72 ppm) are converted into two relatively narrow multiplets in II, with centers at 7.09 and 7.30 ppm.

*Thermolysis of  $\text{Cp}_2(\text{CO})_5\text{Mo}_2(\text{Ph}_2\text{N}_2\text{C})$  (II).* When a toluene solution of II was refluxed for 2.5 h two products were obtained. Whereas the first one proved to be identical with I by means of IR and NMR data, the second one (III) was a mononuclear complex as established by analytical and mass spectroscopic data. Its IR absorptions at 1952, 1858 ( $\nu(\text{CO})$ ) and 1593, 1494, and  $1430\text{ cm}^{-1}$  ( $\nu(\text{NCN})$ ) again point towards the presence of an amidinato ligand attached to a  $\text{Cp}(\text{CO})_2\text{Mo}$  moiety, for they are closely similar to those of II. As in II, the further members of the heterocycle may be two N-phenyl units and the analytical data are consistent with the presence of a cyclopentadiene group bonded to the central carbon atom. The presence of such a group is supported by the  $^1\text{H}$  NMR spectrum of III in which the olefinic character of this part of the molecule is shown by the appearance of multiplets at 2.66, 2.85, 5.98, and 6.24 ppm. The chemical shifts of the  $\text{CH}_2$  protons

and the vinylic protons correspond well to those observed for  $\text{CH}_3\text{C}_5\text{H}_5$  [12] and  $\text{Ph}_3\text{CC}_5\text{H}_5$  [13], respectively. Thus the amidinato atom is preferentially attached to positions 2 or 3 of the cyclopentadiene ring. This isomerism also gives rise to the appearance of two cyclopentadienyl resonances, at 5.56 and 5.58 ppm, respectively. The ratio of the isomers is about 40/60, but, as for the free monosubstituted cyclopentadienes, attribution of the signals to the separate structures is not possible. The 1-isomer seems to be present only in very low concentrations (<1%), and cannot be detected.

## Discussion

The results described extend knowledge of the reactivity of metal imido complexes. Known reactions involve the terminal imido ligand in  $\text{ReCl}_3(\text{NR})(\text{PPh}_3)_2$ , which can be oxidized [14] or reduced [15] under forcing conditions. Other reactions involve the coupling of two RN ligands in  $\text{OsO}_2(\text{t-BuN})_2$  by alkenes [16] or electrophilic addition of  $\text{CH}_3\text{I}$  to  $(\text{C}_5\text{Me}_5)_2\text{VNPh}$  [17]. Of interest for catalysis [18] may be coupling reactions of the capping  $\mu_3$ -ligand in  $\text{Fe}_3(\text{NPh})_2(\text{CO})_9$ , with e.g. carbenes and alkynes [19]. Complex I is the first binuclear complex containing a reactive imido ligand. Knowledge of the reactivity of the  $\eta^2$ -isocyanide bridge can only be drawn from reactivity studies on terminal RNC ligands [20], and there is as yet only a limited number of complexes containing this ligand in the bridging form [4,20].

It is striking that in I the nearly perpendicular arrangement of MoNPh and CNPh groups brings the imido nitrogen relatively close to the isocyanide carbon. Furthermore the semi-bridging CO ligand, which is directed towards the more electropositive Mo atom may represent a "labile" coordination site, which can probably facilitate the first step. Thus, we propose that under the action of an excess of CO the originally "saturated" imido Mo atom may take up one CO ligand, the semi-bridging CO group being converted at the same time into a terminal one. For electronic reasons this step requires transformation of the nearly linear imido ligand into a bent one. In this context it should be noted that bent imido ligands were suggested to show enhanced reactivity [5], but the linear imido unit in  $(\text{C}_5\text{Me}_5)_2\text{VNPh}$  does not react with free isocyanides [17]. On the other hand terminal RNC ligands are susceptible to a nucleophilic attack by amides to produce amidine ligands provided the reaction is facilitated by a positive charge at the metal atom [21]. From these results, and from the results of our X-ray investigation of I, nucleophilic attack of the NPh ligand at the isocyanide C atom seems very likely. In further steps the Mo-N-C-N heterocycle becomes planar and the Mo-Mo bond is broken. The valence changes during these steps are compensated by further CO up-take. Formally the whole process may be regarded as a 2 + 2 cycloaddition of the Mo=N moiety and the  $\text{RN}\equiv\text{C}$  ligand. The thermolytic cleavage of the amidinato group in II leads to two products of different types. For the formation of I the release of CO must be assumed, leaving highly reactive Mo centers which may be best stabilized by the 4e donors PhN and PhNC. This behavior seems to be in contrast to the normally observed thermolytic CO dissociation of carbonyl rich CpMo dimers, which most often lead to an increase in the Mo-Mo bond order [22]. The formation of by-product III may be attributed to heterolytic processes in which the  $\text{CpMo}(\text{CO})_3$  radical formally is displaced by a Cp radical.

The original aim of this work was the incorporation of carbodiimides into the metal-metal triply bonded  $[\text{CpMo}(\text{CO})_2]_2$  by means of an allene-like addition across the  $\text{Mo}\equiv\text{Mo}$  bond [4]. This was finally achieved in an indirect way by carbonylation of I: metalla-amidates and carbodiimides in both have a similar N-C-N skeleton. This relationship is shown also by the fact that carbodiimides can be transferred into metalla-amidates by nucleophilic attack of metal carbonyl anions, e.g.  $[\text{Cr}(\text{CO})_5]^-$  or  $[\text{CpFe}(\text{CO})_2]^-$ . These were finally stabilized as diamino-carbene complexes [23].

In conclusion, the CO promoted insertion of a terminal RN ligand into a RNC bridge provides a unique example of reversible C-N bond formation. Study of the generality of this reaction is in progress in our laboratory, and involves modification of the substituent on the carbodiimide as well as other metal substrates.

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