The minicomputer is interfaced by low-speed data lines to a CYBER 170-855 (NOS operating system) where all computations are performed.

A crystal of dimensions 0.12 mm × 0.12 mm × 0.11 mm was selected and affixed to a goniometer with silicone grease and then transferred to the goniostat where it was cooled to −159 °C for characterization and data collection. (Table IV). A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with monoclinic symmetry which could be indexed as the unique space group $P2_1/c$. From a total of 3448 reflections, 2612 reflections ($F > 3\sigma(F)$) were used in the structure solution and refinement. The structure was solved by direct methods (MULTAN 78) and Fourier techniques and refined by full-matrix least squares. All hydrogen atoms were located and refined isotropically (non-hydrogens anisotropically.) A final difference Fourier was featureless, the largest peak being 0.27 e Å^{-3}. Psi scans of several reflections were flat, and no absorption correction was deemed necessary. Final atomic coordinates and thermal parameters are listed in Table V. Selected bond distances and angles are listed in Table VI.

Kinetics of Endo → Exo Conversion of Allyl Cations II. For the purpose of obtaining rates of conformational equilibration, relative rates of addition, and ESR measurements, substoichiometric amounts of $NOPF_6$ were added to cations IIc and IId. The residual precursor signals (due to Ic and Id) were used as internal standards in NMR experiments. Typical experimental conditions are as follows.

A solution of 38.9 mg (0.135 mmol) of Ic in 1 mL of CH_3CN was treated with 0.062 mmol of $NOPF_6$ (as a standard solution) at −20 °C and stirred 5 min at that temperature. Then, 100 μL of a 0.44 M dimethyl lithiobenzylmalonate solution (in CH_3CN, prepared as described above) was added and stirred quickly, and aliquots of the resultant mixture were transferred to 5.0-mm (o.d.) Pyrex NMR tubes against a countercurrent of argon, frozen at dry ice temperature, and sealed under vacuum. (An appropriate volume of acetonitrile-d_3 or acetone-d_6 was added prior to sealing to provide an internal lock signal.)

Alternatively, a solution of 29.8 mg (0.091 mmol) of Id in 1 mL of CH_3CN was treated with 0.045 mmol of $NOPF_6$ (as a standard solution) at −20 °C and stirred 5 min at that temperature. Then, 5 μL of a 0.40 M NaI solution in CH_3CN was added and stirred quickly, and aliquots of the resultant solution were transferred to either 5.0-mm (o.d.) Pyrex NMR tubes or 1-mm (i.d.) Pyrex ESR tubes, which were frozen at −78 °C and sealed as before.

Acknowledgment. We thank J. C. Huffman for the crystallographic determination of VIII and the National Science Foundation and the Robert A. Welch Foundation for financial support.

Registry No. *exo*-Ia, 100296-52-4; *endo*-Ia, 100296-53-5; *exo*-Ib, 95781-86-5; *endo*-Ib, 95781-86-5; *exo*-Ic, 63976-37-4; *endo*-Ic, 39015-45-7; Id, 81923-02-6; *exo*-IIa, 100296-44-4; *endo*-IIa, 100296-46-6; *exo*-IIb, 100296-48-8; *endo*-IIb, 100296-50-2; *exo*-IIc, 100296-51-3; *endo*-IIc, 100348-11-6; *exo*-IId, 90081-05-3; *endo*-IId, 90129-01-4; III (isomer 1), 100229-40-1; III (isomer 2), 100296-54-6; IV (isomer 1), 100229-41-2; IV (isomer 2), 100348-12-7; V (isomer 1), 100229-42-3; V (isomer 2), 100296-55-7; VI (isomer 1), 100229-43-4; VI (isomer 2), 100296-56-8; VII, 100229-44-5; VIII, 100243-60-5; sodium iodide, 7681-82-5; iodine, 7553-56-2; cyclohexanone, 108-94-1; 2-carbomethoxycyclopentanone, 10472-24-9; malononitrile, 109-77-3; diemthyl benzylmalonate, 49769-78-0; cobaltocene, 1277-43-6.

Supplementary Material Available: Listings of anisotropic thermal parameters, complete bond distances and bond angles, and final observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

Reaction of $(C_5H_5)_2Mo_2(CO)_4$ with Carbodiimides: Structural Characterization of $C_5H_5(CO)_2Mo(CNPh)Mo(NPh)C_5H_5$, a Novel Complex Containing a Terminal Phenylimido and a Bridging Phenyl Isocyanide Ligand, and Its Reaction with $P(OMe)_3$[1]

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Received July 3, 1985

One of the products of the reaction of $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ (Cp = η^5-C_5H_5) with an excess of diphenylcarbodiimide is characterized by X-ray crystallography. The substance crystallizes in the space group $P2_1/c$ with cell constants a = 14.123 (2) Å, b = 12.228 (1) Å, c = 12.772 (1) Å, β = 96.09 (1)°, and V = 2193.2 Å^3. R is 0.023 for 3003 reflections ($I > 4.5\sigma(I)$). The structure is identified as $Cp(CO)_2Mo[\mu\text{-}(\eta^1{:}\eta^2\text{-}C{=}NPh)]Mo(NPh)Cp$ (II) containing an unprecedented combination of a complexed phenylimido ligand and a η^2, ($\sigma + \pi$)-bonded isocyanide bridge. Complex II undergoes a substitution reaction with excess $P(OMe)_3$ to form $Cp(CO)Mo[P(OMe)_3]Mo(CNPh)Mo(NPh)Cp$ and a related compound in which the terminal imido ligand is replaced by an oxo ligand.

Introduction

The addition of small molecules to the metal–metal triple bond in the cyclopentadienylcarbonylmolybdenum derivatives $(\eta^5\text{-}C_5R_5)_2Mo_2(CO)_4$ (R = H, Me) has been the subject of several investigations. Whereas allenes add in a symmetrical fashion across the Mo≡Mo bond,[2] heteroallenes, X=C=Y, give various products depending on the nature of the heteroatoms X and Y. Thus, carbon disulfide is incorporated into $(C_5R_5)_2Mo_2(CO)_4$ (R = H, Me) as a

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0276-7333/86/2305-0655$01.50/0

nonbridging, side-on coordinated ligand, forming compounds of the composition $(C_5R_5)_2Mo_2(CO)_5(CS_2)$.[3] Reaction of $(C_5R_5)_2Mo_2(CO)_4$ with excess MeN=C=S yields mononuclear dithiocarbamato complexes $C_5R_5(CO)_2MoS_2CNHMe$ (R = H, Me). However, their stoichiometric reaction gives the sulfur abstraction product $[C_5Me_5(CO)_2Mo]_2(CNMe)$, bearing a $\sigma + \pi$-bonded isonitrile bridge as the main product.[4]

In a preliminary communication we reported on the reaction of $(C_5H_5)_2Mo_2(CO)_4$ (I) with an excess of carbodiimides RN=C=NR which formed two asymmetrically bridged compounds.[5] The structure of the phenyl isocyanide derivative III (Scheme I) was confirmed by an X-ray analysis.[6] Although the proposed carbodiimide structure for the second product was in good agreement with ^{1}H NMR and IR spectroscopic data, the absence of spectroscopic data on similar compounds did not allow for direct comparison. Moreover, the reversible addition of carbon monoxide to this complex was in accord with a metal–metal bond nature similar to I. In this paper we wish to describe the results of an X-ray diffraction study on II, which reveals that the originally postulated carbodiimide ligand has been cleaved to give an asymmetric isocyanide bridge and a terminal imido ligand. The subsequent reaction of II with $P(OMe)_3$ gives a first insight into the reaction behavior of this novel class of compounds.

Experimental Section

General Data. All procedures were carried out under nitrogen with N_2-saturated, dry 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 run on a Varian 311A instrument. NMR spectra were recorded on a Bruker WH250 instrument. $Cp_2(CO)_2Mo_2(CNPh)(NPh)$ (II) was prepared as described previously from I and a tenfold excess of PhN=C=NPh in toluene at 100 °C.[5]

Preparations. Reaction of II with $P(OMe)_3$. A mixture of 370 mg (0.65 mmol) of II with 0.80 g (6.5 mmol) of $P(OMe)_3$ was refluxed in 100 mL of toluene for 18 h. The solution was cooled to room temperature and concentrated to 10 mL. Chromatography on SiO_2 (column 34 × 4 cm) gave trace amounts of red-brown starting material, eluted with toluene, followed by a violet-red band eluted with toluene/acetone (20:1). Repeated chromatography of this band with toluene/acetone (30:1) as eluent resulted in the isolation of dark red IV (170 mg, 39%) and red-brown V (82 mg, 29%). Recrystallization of both complexes from ether/pentane (1:2) gave dark shiny crystals.

Anal. Calcd for $C_{27}H_{29}N_2O_4PMo_2$ (IV): C, 48.52; H, 4.37; N, 4.19; mol wt, 668.4. Found: C, 48.41; H, 4.38; N, 4.84; mol wt, 660 (^{92}Mo). IV: mp 145 °C dec; IR (KBr) ν_{CO} 1775 (m), ν_{CN} 1543 (s), ν_{PO} 1020, 1005 (m) cm^{-1}.

Anal. Calcd for $C_{21}H_{24}NO_5PMo_2$ (V): C, 42.51; H, 4.08; N, 2.36; mol wt, 593.3. Found: C, 42.32; H, 3.62; N, 2.48; mol wt, 585 (^{92}Mo). V: mp 92 °C dec; IR (KBr) ν_{CO} 1785 (s), ν_{CN} 1550 (s), ν_{PO} 1055, 1010 (m), $\nu_{Mo=O}$ 912 (m) cm^{-1}.

Solution of the Structure of II. A dark red crystal, obtained from an ether solution of II at −35 °C, of approximate dimensions 0.15 × 0.30 × 0.65 mm was used for all X-ray measurements. An Enraf-Nonius CAD-4 automated diffractometer was used with Mo Kα radiation monochromatized by a dense graphite crystal assumed to be ideally imperfect. Final cell constants as well as other information concerning data collection and refinement are given in Table I. From the systematic absences noted, the space group was shown to be $P2_1/c$. Intensities were measured by using the θ–2θ technique, with the scan rate depending on the net count obtained in rapid prescans of each reflection. Two standard reflections were monitored every 2 h and showed no significant variations from the values of the initial measurements. In reducing the data, Lorentz and polarization factors were applied, as well as an empirical absorption correction based on azimuthal psi scans of eight reflections having χ near 90°.[7]

Table I. Crystallographic Data for $Cp_2(CO)_2Mo_2(CNPh)(NPh)$ (II)

space group	$P2_1/c$
cell consts	
a, Å	14.123 (2)
b, Å	12.228 (1)
c, Å	12.772 (1)
β, deg	96.09 (1)
cell vol (calcd for Z = 4), Å^3	2193.23
mol formula	$Mo_2O_2N_2C_{25}H_{20}$
mol wt, g/mol	572.31
d(calcd), g/cm^3	1.7
abs coeff, cm^{-1}	10.47
data collectn range	$4° \leq 2\theta \leq 46°$
scan width	$\Delta 2\theta = 2(1.0 + 0.35 \tan \theta)$
max scan time, s	180
total data collected	3597
data with $I > 4.5\sigma(I)$	3003
total variables	275
$R = \sum \lVert F_o\rvert - \lvert F_c\rVert / \sum \lvert F_o\rvert$	2.3%
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \sum w \lvert F_o\rvert^2]^{1/2}$	2.4%
weights	$\omega = [\sigma(F_o)]^{-2}$
radiatn	λ = 0.71073 Å (Mo Kα)

The structure was solved by interpretation of the Patterson map which gave the coordinates of the two Mo atoms. The remaining atoms were found in subsequent Fourier syntheses and refined isotropically and then anisotropically. At this stage, the image of a second cyclopentadienyl ring appeared in the difference map, slightly displaced with respect to C15–C19. The two rings were refined isotropically as rigid bodies. An occupancy of 20% for the second ring yielded similar temperature factors in the two rings. All hydrogens were calculated ideally. Upon convergence (shifts/esd ratios less than 0.1) the values of the crystallographic parameters were those listed in Table II. The atomic scattering factors used were those of Cromer and Mann[8] except for the hydrogen atoms.[9] Calculations were made by using Molecular Structure Corp.'s Texray 230 modifications of the SDP-PLUS series of programs first and then were carried out on SHELX-76[10] when rigid-body calculations were needed.

Results

Molecular Structure of $Cp(CO)_2Mo(CNPh)Mo(NPh)Cp$ (II). A single crystal X-ray diffraction study was carried out on II, which has been synthesized as reported previously.[5] The atomic parameters and bond lengths and angles are presented in Tables II–IV. Least-squares planes are given in Table VII (supplementary material). An ORTEP drawing of II is shown in Figure 1. The packing of the molecule in the unit cell is displayed in Figure 2 (supplementary material). The result of the structure determination reveals that II does not contain a carbodiimide bridge as previously assumed but rather

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Table II. Atomic Coordinates and Thermal Parameters ($\times10^3$; $\times10^4$ for Mo) for II

atom	x/a	y/b	z/c	$U(11)$	$U(22)$	$U(33)$	$U(12)$	$U(13)$	$U(23)$
Mo1	0.20102 (2)	−0.37916 (2)	0.02909 (2)	315 (2)	284 (2)	253 (2)	23 (1)	53 (1)	24 (1)
Mo2	0.40531 (2)	−0.31667 (2)	0.0512 (2)	33 (0)	35 (0)	27 (0)	−5 (0)	1 (0)	2 (0)
01	0.4533 (2)	−0.5047 (3)	0.2112 (2)	53 (2)	67 (2)	57 (2)	9 (2)	5 (1)	30 (2)
02	0.2894 (2)	−0.2164 (3)	0.2224 (2)	71 (2)	78 (2)	45 (2)	−1 (2)	13 (2)	−25 (2)
N1	0.1878 (2)	−0.4568 (2)	0.1421 (2)	38 (2)	32 (2)	30 (2)	−2 (1)	4 (1)	4 (1)
N2	0.2600 (2)	−0.4787 (2)	0.0774 (2)	30 (2)	40 (2)	32 (2)	2 (1)	5 (1)	−5 (1)
C1	0.4360 (3)	−0.4343 (3)	0.1519 (3)	27 (2)	53 (2)	39 (2)	−5 (2)	2 (2)	4 (2)
C2	0.3216 (3)	−0.2609 (3)	0.1539 (3)	49 (2)	44 (2)	37 (2)	−4 (2)	1 (2)	0 (2)
C3	0.3297 (2)	−0.4226 (3)	−0.0341 (3)	31 (2)	39 (2)	28 (2)	3 (2)	6 (2)	4 (2)
C4	0.2455 (2)	−0.5535 (3)	−0.1619 (3)	33 (2)	33 (2)	29 (2)	4 (2)	−1 (2)	−3 (2)
C5	0.3114 (3)	−0.5599 (4)	−0.2363 (3)	41 (2)	63 (3)	32 (2)	5 (2)	2 (2)	−8 (2)
C6	0.2985 (3)	−0.6329 (4)	−0.3154 (3)	66 (3)	68 (3)	34 (3)	19 (2)	3 (2)	−9 (2)
C7	0.2172 (4)	−0.7024 (4)	−0.3229 (3)	89 (4)	54 (3)	33 (3)	13 (3)	−4 (3)	−14 (2)
C8	0.1542 (3)	−0.6955 (3)	−0.2529 (4)	67 (3)	49 (3)	55 (3)	−11 (2)	−2 (2)	−8 (2)
C9	0.1676 (3)	−0.6197 (3)	−0.1687 (3)	42 (2)	43 (2)	47 (3)	−7 (2)	2 (2)	−5 (2)
C10	0.1385 (3)	−0.2017 (3)	0.0205 (4)	55 (3)	32 (2)	69 (3)	14 (2)	−6 (2)	−1 (2)
C11	0.1585 (3)	−0.2256 (3)	−0.0832 (4)	50 (2)	48 (3)	64 (3)	14 (2)	8 (2)	30 (2)
C12	0.1003 (3)	−0.3113 (4)	−0.1202 (3)	60 (3)	62 (3)	41 (3)	22 (2)	−11 (2)	8 (2)
C13	0.0440 (3)	−0.3419 (4)	−0.0404 (4)	35 (2)	52 (2)	67 (3)	8 (2)	−3 (2)	8 (2)
C14	0.0667 (3)	−0.2718 (3)	0.0449 (4)	49 (2)	53 (3)	57 (3)	19 (2)	20 (2)	5 (2)
C20	0.1642 (3)	−0.4970 (3)	0.2369 (3)	41 (2)	27 (2)	28 (2)	−6 (2)	7 (2)	−2 (2)
C21	0.2349 (3)	−0.5403 (3)	0.3098 (3)	47 (2)	39 (2)	39 (2)	1 (2)	7 (2)	4 (2)
C22	0.2109 (3)	−0.5788 (3)	0.4057 (3)	66 (3)	54 (3)	37 (3)	1 (2)	5 (2)	12 (2)
C23	0.1187 (3)	−0.5741 (3)	0.4293 (3)	78 (3)	52 (3)	35 (2)	−11 (2)	22 (2)	5 (2)
C24	0.0488 (3)	−0.5312 (3)	0.3580 (3)	53 (3)	48 (2)	51 (3)	−14 (2)	25 (2)	−4 (2)
C25	0.0705 (3)	−0.4931 (3)	0.2620 (3)	39 (2)	41 (2)	42 (2)	−7 (2)	7 (2)	−4 (2)
C15	0.4403 (3)	−0.1641 (4)	−0.0555 (4)	46 (1)					
C16	0.4905 (3)	−0.2570 (4)	−0.0868 (4)	41 (1)					
C17	0.5563 (3)	−0.2893 (4)	−0.0006 (4)	44 (1)					
C18	0.5467 (3)	−0.2163 (4)	0.0841 (4)	49 (2)					
C19	0.4751 (3)	−0.1389 (4)	0.0502 (4)	52 (2)					
C15′	0.5066 (11)	−0.1575 (11)	0.0765 (9)	21 (4)					
C16′	0.5654 (11)	−0.2489 (11)	0.0603 (9)	17 (3)					
C17′	0.5396 (11)	−0.2886 (11)	−0.0433 (9)	60 (7)					
C18′	0.4649 (11)	−0.2218 (11)	−0.0911 (9)	38 (5)					
C19′	0.4446 (11)	−0.1408 (11)	−0.0171 (9)	38 (5)					
CE1[a]	0.1016 (3)	−0.2705 (3)	−0.0357 (4)	0 (0)					
CE2[a]	0.5019 (3)	−0.2132 (4)	−0.0017 (4)	0 (0)					
CE2′[a]	0.5042 (11)	−0.2115 (9)	−0.0029 (9)	0 (0)					
H5	0.3501 (3)	−0.4999 (4)	−0.1997 (3)	92 (5)					
H6	0.3200 (3)	−0.6677 (4)	−0.3797 (3)	92 (5)					
H7	0.2388 (4)	−0.7370 (4)	−0.3873 (3)	92 (5)					
H8	0.0939 (3)	−0.7207 (3)	−0.2261 (4)	92 (5)					
H9	0.1076 (3)	−0.6453 (3)	−0.1412 (3)	92 (5)					
H10	0.1705 (3)	−0.1444 (3)	0.0677 (4)	63 (5)					
H11	0.2060 (3)	−0.1872 (3)	−0.1230 (4)	63 (5)					
H12	0.0989 (3)	−0.3458 (4)	−0.1913 (3)	63 (5)					
H13	−0.0039 (3)	−0.4025 (4)	−0.0442 (4)	63 (5)					
H14	0.0367 (3)	−0.2722 (3)	0.1124 (4)	63 (5)					
H15	0.3894 (3)	−0.1234 (4)	−0.1000 (4)	63 (5)					
H16	0.4811 (3)	−0.2934 (4)	−0.1573 (4)	63 (5)					
H17	0.6014 (3)	−0.3524 (4)	0.0004 (4)	63 (5)					
H18	0.5840 (3)	−0.2189 (4)	0.1552 (4)	63 (5)					
H19	0.4529 (3)	−0.0774 (4)	0.0931 (4)	63 (5)					
H15′	0.5086 (11)	−0.1128 (11)	0.1423 (9)	63 (5)					
H16′	0.6160 (11)	−0.2799 (11)	0.1127 (9)	63 (5)					
H17′	0.5689 (11)	−0.3525 (11)	−0.0767 (9)	63 (5)					
H18′	0.4324 (11)	−0.2303 (11)	−0.1641 (9)	63 (5)					
H19′	0.3952 (11)	−0.822 (11)	−0.0288 (9)	63 (5)					
H21	0.3024 (3)	−0.5436 (3)	0.2930 (3)	92 (5)					
H22	0.2614 (3)	−0.6100 (3)	0.4580 (3)	92 (5)					
H23	0.1020 (3)	−0.6019 (3)	0.4987 (3)	92 (5)					
H24	−0.0185 (3)	−0.5278 (3)	0.3756 (3)	92 (5)					
H25	0.0192 (3)	−0.4625 (3)	0.2103 (3)	92 (5)					

[a] CE = centers of the cyclopentadienyl rings.

an as yet unknown combination of an isocyanide and an imido ligand. The two Cp rings as well as the imido and one (terminal) CO group are in a cis arrangement. Two bridging ligands, CO and PhNC, form a pseudoplane which is approximately perpendicular to the mean plane defined by C1–Mo1–Mo2–N1. Compared to other known binuclear complexes containing asymmetric isocyanide bridges (Table V), complex II reveals some striking differences: (i) the cis arrangement of Cp ligands in II is unique; (ii) no other complex contains a semibridging pair of RNC and CO ligands; (iii) the C–N bond (1.274 (4) Å) in II is longer than in the other compounds, giving rise to an originally unexpected low ν_{CN} frequency at 1602 and 1580 cm^{-1} in the IR spectrum. As can be seen from Table V this distance is of the same order as in triply bridging, six-electron donor isocyanides. Another indication of enhanced π-interaction between the isocyanide and Mo1 is the fact that the C–N bond is on average 0.13 Å closer to Mo1 than in

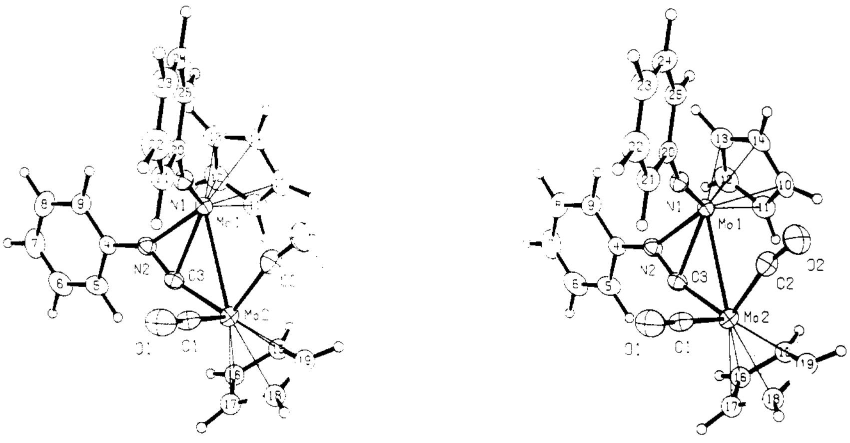

Figure 1. Stereoscopic view of the molecule of II.

Table III. Selected Bond Lengths (Å) for II

Mo1-Mo2	2.969 (1)	N2-C3	1.274 (4)
Mo1-N1	1.754 (2)	N2-C4	1.411 (4)
Mo1-N2	2.067 (2)	Mo2-C1	1.946 (4)
Mo1-C2	2.637 (3)	Mo2-C2	1.976 (4)
Mo1-C3	2.135 (3)	Mo2-C3	1.940 (3)
Mo1-C10	2.342 (3)	Mo2-C15	2.394 (3)
Mo1-C11	2.402 (3)	Mo2-C16	2.356 (4)
Mo1-C12	2.402 (3)	Mo2-C17	2.324 (4)
Mo1-C13	2.345 (3)	Mo2-C18	2.344 (4)
Mo1-C14	2.331 (3)	Mo2-C19	2.387 (4)
Mo1-CE1[a]	2.043 (3)	Mo2-CE2[a]	2.029 (4)
N1-C20	1.383 (4)		
C1-O1	1.155 (4)		
C2-O2	1.388 (4)		

[a] CE1 and CE2 are the ring centroids of C10-C14 and C15-C19, respectively.

Table IV. Selected Bond Angles and Torsional Angles (deg) for II

N1-Mo1-Mo2	104.3 (1)	C1-Mo2-Mo1	91.1 (1)
N2-Mo1-Mo2	76.0 (1)	C2-Mo2-Mo1	60.6 (1)
N2-Mo1-N1	108.1 (1)	C2-Mo2-C1	85.7 (2)
C2-Mo1-Mo2	40.7 (1)	C3-Mo2-Mo1	45.9 (1)
C2-Mo1-N1	85.3 (1)	C3-Mo2-C2	105.8 (2)
C2-Mo1-N2	116.1 (1)	C3-Mo2-C1	87.1 (1)
C3-Mo1-Mo2	40.7 (1)	CE2-Mo2-Mo1	144.1 (2)
C3-Mo1-N1	110.3 (1)		
C3-Mo1-N2	35.3 (1)	C20-N1-Mo1	166.3 (3)
C3-Mo1-C2	81.0 (1)	C4-N2-C3	136.2 (3)
CE1-Mo1-Mo2	119.3 (2)	Mo2-C1-O1	179.2 (3)
		Mo2-C2-O2	165.6 (4)
CE1-Mo1-Mo2-CE2	-20.1	Mo2-C3-N2	162.9 (3)
CE1-Mo1-Mo2-C2	78.7		
N1-Mo1-Mo2-C2	-64.7		
N1-Mo1-Mo2-CE2	-163.6		
N2-Mo1-Mo2-CE2	91.1		
N2-Mo1-Mo2-C1	-85.7		

$(C_5H_5)_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{-}C_6H_5NC)$.[13]

Similar observations can be made in the complex $C_5H_5(CO)[P(OMe)_3]Mo(CNPh)MoOC_5H_5$ (V), which is one of the products of the reaction of II with $P(OMe)_3$. A preliminary X-ray diffraction study[14] on this complex reveals a Mo-Mo bond length of 2.928 (2) Å as well as an extremely long C-N distance (1.32 (2) Å) which results in a low ν_{CN} frequency at 1550 cm^{-1} in the IR spectrum. This observation is not surprising in view of the similar strong π-bonding ability of oxo (O) and imido (NR) ligands.[15,16]

Following the proposal of Curtis[17] the isocyanide as well as the carbonyl group C2-O2 can be regarded as four-electron donor semibridging ligands. It is of interest that in II their π-interactions are simultaneously directed toward Mo1, probably in order to diminish the polarization of the Mo-Mo single bond due to the terminal imido ligand. The found Mo-Mo distance of 2.969 (1) Å is still within the Mo-Mo single bond region, which is in agreement with a formal electron count, when both the imido and the isocyanide ligand are considered as four-electron donors. The fact that it is ca. 0.3 Å shorter than in the only isocyanide-bridged species III (d(Mo-Mo) = 3.212 Å)[6,13] or in the unbridged compound $Cp_2Mo_2(CO)_5CNMe$ (d(Mo-Mo) = 3.230 Å)[18] may be attributed to the imido ligand.

The Mo1-N1-C20 angle (θ = 166.3°) reflects the triple-bond character of the Mo1-N1 linkage. A value for the metal-N-R bond angle less than 180° is very common for organoimido ligands.[15,16,19] The found distance of 1.754 (2) Å for the molybdenum-nitrogen triple bond compares well with the two known examples available from the literature for nearly linear Mo≡NPh (1.734 and 1.754 Å).[16]

Reaction of IIb with $P(OMe)_3$. Two products could be isolated from the reaction, in toluene at 100 °C, of II with a tenfold excess of $P(OMe)_3$ (Scheme I). Analytic and spectroscopic data indicate that a carbonyl group in II has been substituted by a $P(OMe)_3$ ligand. The IR spectrum exhibits a single ν_{CO} frequency at 1775 cm^{-1} in accord with the loss of the terminal CO group (ν_{CO} = 1895 cm^{-1}) in II.[20] Apparently, the isocyanide bridge has preserved its original $\sigma + \pi$ coordination mode, but the electronic influence of the incoming ligand gives rise to increased π-interaction, as can be deduced from a lowering of the corresponding ν_{CN} frequency from 1580 cm^{-1} in II to 1543 cm^{-1} in IV. The ^1H NMR spectrum consists of a singlet at 5.72 ppm and of a doublet at 5.23 ppm for the

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[20] The nitrene metal-nitrogen stretching, which generally falls in the range 1000-1150 cm^{-1}, is frequently obscured, and coupling with other metal ligand modes further complicates the situation.[15]

Table V. Bond Parameters and IR Frequencies of Various $\sigma + \pi$-Bridging Isocyanide Ligands

complex	geometry	e	d_{C-N}, Å	ν_{C-N}, cm^{-1}	ref
$(C_5H_5)_2Mo_2(CO)_4(PhNC)$ (monoclinic)	μ_2-η^2	4	1.244 (3)	1666	13
$(C_5H_5)_2Mo_2(CO)_4(PhNC)$ (triclinic)	μ_2-η^2	4	1.234 (9)	1677	5, 6
$(C_5Me_5)Mo_2(CO_4)(MeNC)$	μ_2-η^2	4	1.17 (3)	1725	4
$(C_5H_5)_2(CO)_2Mo_2(CNPh)(NPh)$	μ_2-η^2	4	1.274 (4)	1602, 1580	this work
$(C_5H_5)_2(CO)[P(OMe)_3]Mo_2(PhNC)O$	μ_2-η^2	4	1.32 (2)	1550	this work
$Mn_2(CO)_4(Ph_2PCH_2PPh_2)$($p$-TolNC)	μ_2-η^2	4	1.25 (1)	1661	*a*
Nb_3Cl_8(t-BuNC)$_5$	μ_3-η^2	6	1.31 (1)		*b*
$Fe_3(CO)_9$(t-BuNC)	μ_3-η^2	6	1.270 (5)	1553	*c*
$Ru_5(CO)_{14}$(t-BuNC)$_2$	μ_5-η^1	6	1.375 (8)		*d*

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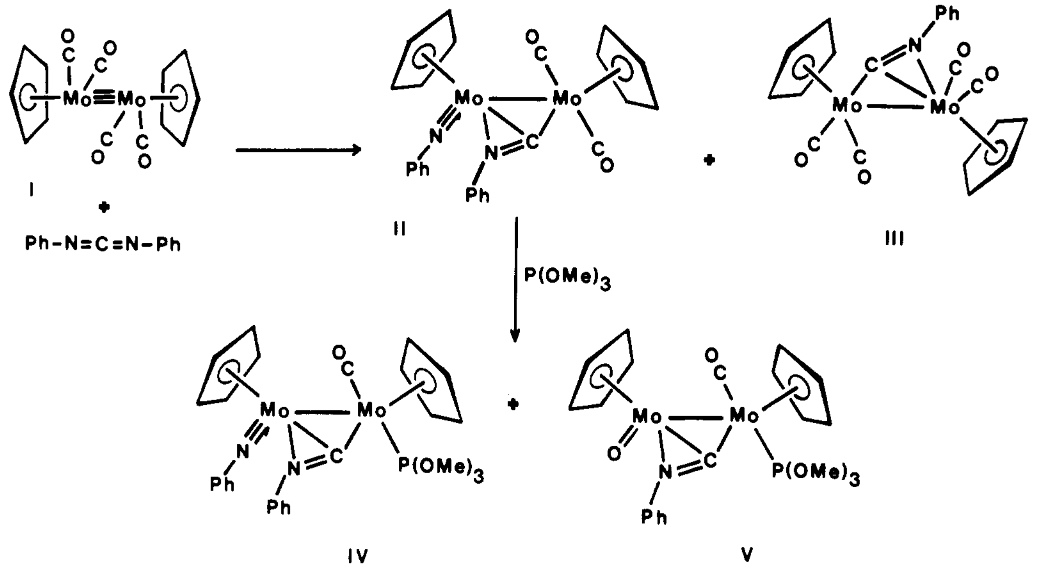
Scheme I



C_5H_5 protons. The range and the pattern of the aromatic protons are very similar to II.

By contrast, elemental analysis, ^1H NMR, and mass spectral data confirmed the loss of one phenyl group for the second product V. The IR absorptions at 1785 (ν_{CO}) and 1550 cm^{-1} (ν_{CN}) are similar to those of complex IV, while the strong absorption at 912 cm^{-1} can be assigned to a $\nu_{Mo=O}$ frequency with the aid of preliminary crystallographic results.[14] This study shows V to have a structure similar to II, except that the terminal nitrene and carbonyl ligands have been replaced by an oxo and a $P(OMe)_3$ ligand, respectively. In this context it should be noted again that oxo and imido ligands possess a comparable strong π-bonding ability.[15,16] The source of oxygen is not yet clear, but it cannot be excluded that $P(OMe)_3$ itself serves as oxygen donor. Attempts to extend this reaction to other nucleophiles, such as $PhP(OMe)_2$, PPh_3, PBu_3, and $PhCH_2NC$ were uniformly unsuccessful. In spite of a large excess of ligand and extended reflux in toluene complex II was recovered unchanged in each case.

^{1}H NMR Spectra. On the basis of the X-ray structures now available for II and V, more definitive assignments for the ^1H NMR signals of the aromatic protons can be made for all compounds described in this paper (Table VI). Obviously, the chemical shifts of the phenyl hydrogens are very sensitive to the chemical environment of molybdenum. Comparison of the spectra of III[13] and V demonstrates that chemical shifts of 7.2, 7.5, and 7.8 ppm are characteristic of isocyanide phenyl protons. A downfield shift for the ortho and meta protons may be a consequence of the increased π-donation from PhNC to Mo. Two corresponding sets of signals at about 7.8 and 7.5 ppm can be unequivocally located for II and V; however, the signal at 7.2 ppm is buried by overlapping resonances of the imido ligand (7.25–6.88 ppm). The aromatic resonances of II and V are shifted significantly upfield compared to Re compounds. For example, the phenyl protons of $Re(NPh)(S_2CNMe_2)_3$ appear at 7.7, 7.5, and 7.2 ppm.[21]

Table VI. ^1H NMR Spectroscopic Data for Complexes II–V ($CDCl_3$ Solution; Internal Me_4Si)[a]

compd	δ_{CH_3O} (J_{P-H})	$\delta_{C_5H_5}$ (J_{P-H})	$\delta_{C_6H_5}$ ($J_{^3H-H}$)
II		5.40 (s), 5.70 (s)	6.89–7.24 (m),[b] 7.50 (dd, 7.3, 8.1), 7.84 (d, 8.1)
III		5.42 (s), 5.44 (s)	7.21 (d, 7.0), 7.40 (dd, 8.1, 7.0), 7.50 (d, 8.1)
IV	3.17 (d, 11.81)	5.23 (d, 0.72), 5.72 (s)	6.88–7.21 (m),[b] 7.43 (dd, 8.0, 7.5), 7.74 (d, 8.0)
V	3.41 (d, 11.82)	5.26 (d, 0.84), 5.77 (s)	7.17 (d, 7.5), 7.47 (dd, 8.2, 7.5), 7.83 (d, 8.25)

[a] s = singlet, d = doublet, m = multiplet; coupling constants in Hz. [b] See text.

Conclusion

Only few examples are known in which carbodiimides coordinate onto transition-metal complexes as an intact ligand in a η^1- or η^2-mode.[22] Hydride transfer from $H_2Os_3(CO)_{10}$ to diisopropylcarbodiimide provides an example

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in which the intact ligand skeleton has been broken down.[23] For the transformation of carbodiimides RN=C=NR into isonitrile and dehydroguanidinium complexes ligand dimerization has been found to be the key step, thus excluding the existence of a free nitrene intermediate.[24] Relatedly it is of interest that the stabilization of an imido ligand has been achieved in II. The simultaneous presence of the imido and the isocyanide ligand may be indicative of the elusive carbodiimide-bridged molybdenum dimer, which appears to be too labile under these stereochemical constraints. This point will be the subject of further investigations.

Acknowledgment. We thank the Robert A. Welch Foundation for research support (Grant E-594). Acknowledgement is also made to the E.S.C.I.L. (France) for giving to M.D. the opportunity to come to Houston.

Registry No. II, 87994-12-5; IV, 100334-22-3; V, 100334-23-4; $P(OMe)_3$, 121-45-9; Mo, 7439-98-7.

Supplementary Material Available: Tables of full bond lengths and bond angles, least-squares planes and dihedral angles (Table VII), and structure factors for II and a stereoscopic view (Figure 2) of the unit cell packing (22 pages). Ordering information is given on any current masthead page.

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Energetics of Transition-Metal–Sulfur and –Oxygen Bonds in $M(\eta^5\text{-}C_5H_5)_2L_2$ Complexes (M = Ti, Mo, W). Molecular Structure of $Mo(\eta^5\text{-}C_5H_5)_2(SO_4)$

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Received June 21, 1985

The energetics of transition-metal–sulfur bonds in bis(η^5-cyclopentadienyl)bis(thiolato)metal complexes, $M(\eta^5\text{-}C_5H_5)_2(SR)_2$ (M = Mo, W, Ti), has been reinvestigated and compared with reevaluated metal–oxygen data on the same type of molecules. Bond enthalpy terms, $E(\text{Mo–SR})$ (R = $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, $t\text{-}C_4H_9$, and $n\text{-}C_{10}H_{21}$), which were obtained by using calorimetric values for the standard enthalpies of formation of the complexes, confirm a strong steric effect in the case of $t\text{-}C_4H_9S$ and indicate an increase in metal–sulfur bond strength with the length of the n-alkyl chain, $E(\text{Mo–SC}_{10}H_{21}\text{-}n) \gtrsim E(\text{Mo–SC}_4H_9\text{-}n) \gtrsim E(\text{Mo–SC}_3H_7\text{-}n)$. The thermochemistry of the complex $Mo(\eta^5\text{-}C_5H_5)_2(SO_4)$ was also studied, leading to $E(\text{Mo–O}) \approx 338 \pm 13$ kJ mol^{-1}. This value excludes noticeable strain on the metallacycle, since it compares with other molybdenum–oxygen bond enthalpy terms. The molecular structure of the sulfate complex, which was also determined in the present study, is compatible with the Mo–O bond enthalpy. The structural data were obtained by X-ray diffraction and show bidentate coordination of the sulfate ligand, with O–Mo–O = 66.1 (2)° and Mo–O = 211.3 (3) pm. The angle O–S–O = 98.3 (2)° (coordinated oxygen) shows a small distortion of this moiety, and extended Hückel calculations show that the rigidity of the SO_4 geometry is responsible for the small O–Mo–O angle. The sulfate complex crystallizes in the orthorhombic space group *Cmcm* with four molecules per unit cell; the lattice constants are a = 935.6 (5) pm, b = 854.7 (2) pm, and c = 1297.9 (4) pm.

Introduction

Early studies on the chemistry of transition-metal molecules containing metal–sulfur bonds were fostered by the growing interest in heterogeneous catalytic problems. This can be illustrated by studies involving metal sulfides, which are used as catalysts in many industrial processes.[1] Among these, sulfur removal from petroleum-based feedstocks through hydrodesulfurization (HDS) reactions[2] is of particular importance, not only to minimize environmental problems but also because sulfur inhibits the activity of many catalysts.[3-5] This led to detailed investigations about the HDS reactions mechanisms, which often include the formation or the cleavage of transition-metal–sulfur bonds,[2,6-9] and also to the study of "poisoning" processes, usually associated with the formation of sulfur products at the catalyst surface.[4,5,10]

Several recent studies on transition-metal complexes containing metal–sulfur bonds explore the general advantages[11] of homogeneous over heterogeneous catalysis.

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