(III) dimer is produced during the reduction of the Pt(III) head-to-head dimer, the reactions (2) and (3) are probably involved in the electrochemical generation of PPB.

$$\mathrm{Pt^{III}\text{–}Pt^{III}} + e^- \overset{E_{1/2}{}^1}{\rightleftharpoons} \mathrm{Pt^{II}\text{–}Pt^{III}} + e^- \overset{E_{1/2}{}^2}{\rightleftharpoons} \mathrm{Pt^{II}\text{–}Pt^{II}} \qquad (2)$$

$$\mathrm{Pt^{II}\text{–}Pt^{III}} + \mathrm{Pt^{II}\text{–}Pt^{II}} \rightleftharpoons \mathrm{Pt^{II}\text{–}Pt^{III}\text{–}Pt^{II}\text{–}Pt^{II}}\ (\mathrm{PPB}) \qquad (3)$$

In the multistep charge-transfer reactions of this type, self-exchange reactions must also be considered:[30a]

$$\mathrm{Pt^{II}\text{–}Pt^{II}} + \mathrm{Pt^{III}\text{–}Pt^{III}} \overset{K_c}{\rightleftharpoons} 2\mathrm{Pt^{II}\text{–}Pt^{III}} \qquad (4)$$

The estimated value of $\Delta E_{1/2}$ can be used to calculate the comproportionation constant (K_c) for the system at equilibrium. The equilibrium constant can be estimated[30a] by using the relationship (5). If it is assumed that the difference in

$$K_c = \frac{[\mathrm{Pt^{II}\text{–}Pt^{III}}]^2}{[\mathrm{Pt^{II}\text{–}Pt^{II}}][\mathrm{Pt^{III}\text{–}Pt^{III}}]} = \exp(n_1 n_2 F \Delta E^\circ / RT) \qquad (5)$$

the standard reduction potentials (ΔE°) for the two-step process is $\sim\Delta E_{1/2}$, the calculated value for K_c is in the range $3 < K_c < 7$. This approximate value for K_c suggests that the formation of the mixed-valent $\mathrm{Pt^{II}\text{–}Pt^{III}}$ species is thermodynamically favorable. Although further studies on the kinetics of these reactions will be required to determine the importance of the $\mathrm{Pt^{II}\text{–}Pt^{III}}$ complex in the formation of PPB, it is noteworthy that a $(\mathrm{Pt^{II}\text{–}Pt^{III}})_2$ compound has been obtained from the reactions of *cis*-diammineplatinum(II) with α-pyrrolidone, compound **6**.[24]

Quasi-reversible behavior is observed in the CV studies of pure samples of PPB, and exhaustive electrolysis at +0.80 V results in a net loss of 0.67 electron/platinum atom. These experiments also suggest that the Pt(III) head-to-head dimer is produced upon oxidative electrolysis. A similar result was found in earlier potentiometric studies of PPB. Two independent reports[1e,35] on $\mathrm{Ce^{IV}}$ titrations of PPB suggested that Pt(III) species were produced during the redox titrations. The results presented here confirm these earlier observations.

Conclusion

Structural and electrochemical studies show that metal–metal-bonded Pt(III) dimers can be prepared from the oxidation of both the head-to-tail α-pyridonate-bridged platinum(II) dimer (**5**) and *cis*-diammineplatinum α-pyridone blue (PPB). Electrochemical studies show that metal–metal bond formation in the head-to-tail dimer proceeds through a concerted two-electron charge-transfer process which is coupled to a chemical reaction. In the head-to-head dimer, the metal–metal bond in the platinum(III) complex appears to form through two one-electron steps which are also coupled to a chemical reaction. In this case the coupled chemical reaction may involve the formation of PPB through a multistep process.

Acknowledgment. This work was supported by National Institutes of Health Research Grant CA-15826. We thank Engelhard Industries for a loan of K_2PtCl_4 used to make all platinum complexes.

Registry No. **1**, 86308-22-7; **2**, 86362-05-2; **3**, 62782-86-9; **5**, 76775-76-3.

Supplementary Material Available: Listings of atomic positional and thermal parameters for compounds **1** and **2** (Tables S1 and S2) as well as final observed and calculated structure factors (Tables S3 and S4) (33 pages). Ordering information is given on any current masthead page.

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Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

Bimetallic Aryldiazenido Complexes. Crystal and Molecular Structure of $(\eta^5\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}NNC_6H_4CH_3)Re(CO)_2(\eta^5\text{-}C_5H_5)$ Possessing a μ-Aryldiazenido-*N*,*N′* Bridge

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Received November 30, 1982

The title compound has been synthesized from the reaction of $CpMo(CO)_2(p\text{-}N_2C_6H_4CH_3)$ (Cp = $\eta^5\text{-}C_5H_5$) with $CpRe(CO)_2(THF)$ (THF = tetrahydrofuran) and its structure determined by X-ray crystallography. It crystallizes in space group $P\bar{1}$ with $a = 11.201$ (3) Å, $b = 10.117$ (3) Å, $c = 12.282$ (4) Å, $\alpha = 115.34$ (3)°, $\beta = 118.11$ (2)°, $\gamma = 94.34$ (3)°, and $Z = 2$. The calculated and measured densities are 2.055 and 2.08 (1) g cm^{-3}, respectively. On the basis of 2525 observed X-ray-counter-measured intensities with $I \geq 2.3\sigma(I)$ in the range $45° \geq 2\theta$ (Mo Kα), the structure was solved and refined by full-matrix least-squares methods to $R = 0.024$ and $R_w = 0.033$. The bimetallic complex may be described as a $Cp(CO)_2Mo(NNC_6H_4CH_3)$ molecule coordinated through the exo nitrogen atom (N′) of its singly bent aryldiazenido ligand to a $CpRe(CO)_2$ fragment. The MoNN′ skeleton remains essentially linear. Important dimensions are Mo–N(2) = 1.822 (4) Å, Re–N(1) = 2.152 (4) Å, N(1)–N(2) = 1.256 (6) Å, Mo–N(2)–N(1) = 177.7 (4)°, and Re–N(1)–N(2) = 118.9 (3)°.

Introduction

In mononuclear complexes, organodiazenido ligands (N_2R) (R = alkyl or aryl) have been found to exhibit two common structural types: the "singly bent" structure (A) where N_2R is formally a 3-electron donor and the "doubly bent" structure (B) where N_2R is formally a 1-electron donor.

With these as a basis, a number of potential structures for bimetallic organodiazenido complexes can be visualized, such as C–E. Structure D has been found to occur in the aryldiazenido complexes $Mn_2(CO)_8(N_2Ph)_2$,[1] $HOs_3(CO)_{10}(p$-

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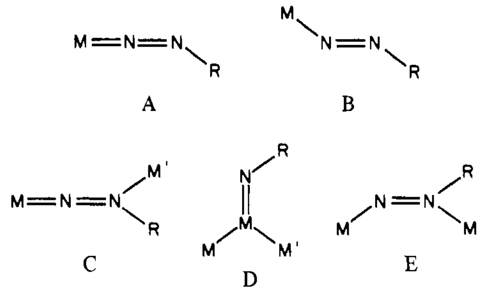

$N_2C_6H_4CH_3)$,[2a] $[\{IrNO(PPh_3)\}_2O(o\text{-}N_2C_6H_4NO_2)]^+$,[3] and $[Pd_2Cl_2(dppm)_2(p\text{-}N_2C_6H_4F)]^+$.[4] Structure E is presently not known.[2b] This paper reports the synthesis and X-ray structural characterization of a bimetallic *aryl*diazenido complex conforming to structure C. A similar structure has been proposed for related *alkyl*diazenido complexes and was subsequently verified crystallographically.[5]

Experimental Section

All manipulations were carried out in standard Schlenkware, connected to a switchable inert-atmosphere/vacuum supply, and were conducted under nitrogen. Solvents were dried and purified by standard methods (tetrahydrofuran, THF, by reflux with sodium and benzophenone) and freshly distilled under nitrogen. Decacarbonyldirhenium (Strem Chemicals) was used directly as purchased. Spectra were recorded on the following spectrometers: IR, Perkin-Elmer Model 599B; ^1H NMR, Varian XL-100 (100 MHz) modified for Fourier-transform spectroscopy, in acetone-d_6, using tetramethylsilane as an internal standard; MS, Hewlett-Packard Model 5985 operating at 14 eV. Microanalyses were performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University. The complexes $CpMo(CO)_2(p\text{-}N_2C_6H_4CH_3)$,[6] $CpRe(CO)_3$,[7] and $CpRe(CO)_2(THF)$[8,9] were prepared by published methods (Cp = $\eta^5\text{-}C_5H_5$).

Preparation of $(\eta^5\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}NNC_6H_4CH_3)Re(CO)_2(\eta^5\text{-}C_5H_5)$. To a solution of $CpMo(CO)_2(p\text{-}N_2C_6H_4CH_3)$ (**1**, 75 mg, 0.22 mmol) in THF (20 mL) was slowly added solid $CpRe(CO)_2(THF)$ (85 mg, 0.22 mmol), and the mixture was stirred for 24 h at room temperature. An IR spectrum of the solution at this stage showed the presence of unreacted molybdenum complex, some $CpRe(CO)_3$ (from decomposition of the THF adduct $CpRe(CO)_2(THF)$), and the desired product. The solution was evaporated to dryness under vacuum at room temperature to yield a dark red oil, which was dissolved in benzene (1 mL) and passed through a silica gel column prepared in benzene. Elution with benzene afforded first a dark red band that was identified as the molybdenum aryldiazenido complex (**1**). The second band (yellow) was $CpRe(CO)_3$. The final band (dark red), which was the desired product (**2**), was collected under nitrogen and evaporated in vacuo to dryness to give a dark red oil. Dissolving this in hexane and cooling to −12 °C (freezer) gave the product as dark red crystals (yield 40% based on $CpMo(CO)_2(p\text{-}N_2C_6H_4CH_3)$), mp 133 °C. Anal. Calcd for $(\eta^5\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}N_2C_6H_4CH_3)\text{-}Re(CO)_2(\eta^5\text{-}C_5H_5)$: C, 39.19; H, 2.64; N, 4.35. Found: C, 39.49; H, 2.50; N, 4.34. IR (hexane): ν(CO) 2008 s, 1945 vs, 1920 vs, 1858 vs cm^{-1}. ^1H NMR (acetone-d_6): δ 7.48 d, 7.17 d (4 H, C_6H_4), 6.15 s (5 H, $Mo[C_5H_5]$), 5.10 s (5 H, $Re[C_5H_5]$), 2.34 s (3 H, CH_3).

Table I. Crystal Data for $(\eta^5\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}NNC_6H_4CH_3)Re(CO)_2(\eta^5\text{-}C_5H_5)$

formula weight	643.52
formula	$C_{21}H_{17}ReMoN_2O_4$
space group	$P\bar{1}$
a, Å	11.201 (3)
b, Å	10.117 (3)
c, Å	12.282 (4)
α, deg	115.34 (3)
β, deg	118.11 (2)
γ, deg	94.34 (3)
V, $Å^3$	1040.21
Z	2
D_{obsd}, g cm^{-3}	2.08 (1)
D_{calcd}, g cm^{-3}	2.055
cryst dimens, mm	0.08 × 0.09 × 0.10
μ, cm^{-1}	65.10
radiation	Mo Kα (graphite monochromated)
temp, °C	22
takeoff angle, deg	3
scan type	symmetrical θ–2θ
scan speed, deg min^{-1}	2
scan range, deg	$1.7 + 0.692 \tan \theta$
bkgd count time	40% (scan time) each side (stationary crystal, stationary counter)
2θ limits, deg	3.5–45
reflcns measd	2726
reflcns obsd ($I \geq 2.3\sigma(I)$)	2525
range of transmission coeff	0.34–0.44
no. of variables	262
R	0.024
R_w	0.033

X-ray Structure Determination. A crystal of **2** suitable for data collection was mounted in a Lindemann glass capillary. Weissenberg and precession photographs were used to obtain approximate unit cell dimensions and to define the space group as $P1$ or $P\bar{1}$. Subsequent successful structure solution confirmed the space group to be $P\bar{1}$. Accurate cell dimensions were determined by least-squares refinement of the diffractometer angles of 24 accurately centered reflections with $33.5° \leq 2\theta \leq 36.9°$ distributed over a wide range of reciprocal space (λ(Mo Kα_1) = 0.70926 Å). Data were collected on an automatic Picker FACS-I four-circle diffractometer with a graphite monochromator and a scintillation counter with pulse height discrimination. Crystallographic data and conditions are given in Table I. Standard reflections showed a very gradual decrease (ca. 4%). Lorentz, polarization, scale, and absorption corrections have been applied.

The Re and Mo atoms were located via Patterson synthesis. All other non-hydrogen atoms were located in a subsequent difference-Fourier synthesis. Aryl hydrogen atoms were included in refinement as fixed contributions in their calculated positions. The methyl group hydrogen atoms were not located.

Gauss–Seidel block-diagonal least-squares refinement, with anisotropic temperature factors for all non-hydrogen atoms and isotropic temperature factors (derived from parent carbon atoms) for hydrogen atoms, gave final agreement factors of $R = 0.024$ $[R = \sum||F_o| - |F_c||/\sum|F_o|]$ and $R_w = 0.033$ $[R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}]$ for 262 variables. The largest shift:error during the final cycle was 0.07. The final difference-Fourier map was flat, apart from two peaks (1.2 (1) and 1.5 (1) e $Å^{-3}$) and a trough (−1.1 (1) e $Å^{-3}$) close to the Re atom. These can probably be attributed to deficiences in our absorption corrections due to the irregular crystal shape. In order to eliminate trends in the average $w\Delta^2$ a weighting scheme $w = 1/\sigma(F_o^2) + 0.0008F_o^2$ was adopted for the final cycles of refinement.

Atomic scattering factors, including anomalous dispersion, were taken from ref 10. The computer programs used here were those of ref 11. Final positional parameters are given in Table II and selected bond lengths and angles in Table III. Additional dimensions, anisotropic thermal parameters, mean-plane data, and structure factor

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Table II. Atomic Parameters x, y, and z and B_{eq} for $(\eta^5\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}NNC_6H_4CH_3)Re(CO)_2(\eta^5\text{-}C_5H_5)$[a]

atom	x	y	z	B_{eq},[b] Å^2
Re	0.295635 (21)	−0.066149 (22)	0.179070 (21)	2.789 (9)
Mo	0.40800 (5)	0.38850 (5)	0.20006 (4)	2.393 (18)
O1	0.5797 (5)	1.1833 (5)	0.4530 (4)	4.56 (22)
O2	0.4516 (5)	0.7272 (5)	0.0820 (5)	6.17 (24)
O4	0.1944 (5)	0.4053 (6)	−0.0695 (5)	5.53 (24)
O5	0.1852 (4)	0.4508 (5)	0.2816 (4)	4.89 (22)
N1	0.2826 (4)	0.0324 (5)	0.0512 (4)	2.59 (18)
N2	0.3316 (4)	0.1781 (5)	0.1126 (4)	2.64 (18)
C1	0.4734 (6)	1.0890 (7)	0.3435 (6)	3.8 (3)
C2	0.3937 (6)	0.8102 (6)	0.1185 (6)	3.36 (24)
C4	0.2706 (6)	0.3987 (6)	0.0284 (6)	3.24 (25)
C5	0.2661 (6)	0.4265 (6)	0.2515 (6)	3.10 (24)
C31	0.2176 (7)	−0.0712 (8)	0.3165 (7)	5.0 (3)
C32	0.1923 (6)	−0.2271 (8)	0.2175 (7)	5.1 (3)
C33	0.0868 (6)	−0.2620 (7)	0.0742 (7)	4.2 (3)
C34	0.0522 (6)	−0.1302 (8)	0.0886 (7)	4.7 (3)
C35	0.1308 (7)	−0.0109 (8)	0.2381 (8)	5.5 (3)
C61	0.6002 (6)	0.5408 (7)	0.2283 (6)	3.7 (3)
C62	0.5776 (6)	0.6382 (7)	0.3341 (7)	3.6 (3)
C63	0.6074 (6)	0.5854 (7)	0.4309 (6)	3.3 (3)
C64	0.6507 (6)	0.4567 (7)	0.3849 (6)	3.7 (3)
C65	0.6464 (6)	0.4285 (8)	0.2585 (7)	4.2 (3)
C71	0.2250 (5)	−0.0515 (6)	−0.1044 (5)	2.87 (22)
C72	0.1191 (6)	−0.1967 (6)	−0.1947 (5)	2.94 (23)
C73	0.0545 (6)	−0.2712 (7)	−0.3428 (6)	3.4 (3)
C74	0.0964 (6)	−0.2038 (7)	−0.4030 (6)	3.6 (3)
C75	0.2087 (8)	−0.0634 (8)	−0.3082 (7)	5.2 (3)
C76	0.2717 (7)	0.0141 (7)	−0.1601 (6)	4.1 (3)
C77	0.0253 (9)	−0.2876 (9)	−0.5664 (7)	5.7 (4)

[a] Esd's in parentheses refer to the last digit printed. [b] All atoms have anisotropic thermal parameters (see supplementary data): $B_{eq} = 8\pi^2[(U_{11}^2 + U_{22}^2 + U_{33}^2)/3]^{1/2}$. The error quoted for B_{eq} is the mean of the errors determined for U_{11}, U_{22}, and U_{33}.

listings are available as supplementary data.

Results and Discussion

The molybdenum complex $CpMo(CO)_2(p\text{-}N_2C_6H_4CH_3)$ (**1**) was the first aryldiazenido (aryldiazo) complex to be synthesized, almost 20 years ago.[6] Because of the interest subsequently aroused in organodiazo–transition-metal compounds, numerous other examples have been synthesized and characterized, and the elements molybdenum and tungsten have figured prominently in such compounds. Yet, surprisingly, the chemistry of the prototype compound **1** is largely unexplored, and indeed, its crystal structure has not been published (though that of a closely related molecule in which Cp is replaced by hydridotris(1-pyrazolyl)borate, i.e., $(HB(pz)_3)Mo(CO)_2(N_2C_6H_5)$, has been).[12] By analogy with the latter, as well as from the ν(NN) value[6,13] and 18-electron-counting arguments, the aryldiazenido ligand in **1** undoubtedly is of the 3-electron-donor, singly bent type (structure A). As such, it possesses an unshared electron pair in formally an sp^2-hybrid orbital on N′. In this work we were interested to determine whether this electron pair would be sufficiently basic, in such a neutral *aryl*diazenido complex, to bind to a second transition metal. The rhenium complex $CpRe(CO)_2(THF)$, which can (by facile loss of THF) be regarded as furnishing the 16-electron-intermediate $CpRe(CO)_2$, does indeed react with **1** under mild conditions to generate the bimetallic title complex $(\eta^5\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}NNC_6H_4CH_3)Re(CO)_2(\eta^5\text{-}C_5H_5)$ (**2**). An *alkyl*diazenido complex of tungsten structurally related to **1**, which might, if anything, be expected to be more basic than **1**, gives related bimetallic alkyldiazenido complexes in a similar fashion.[5]

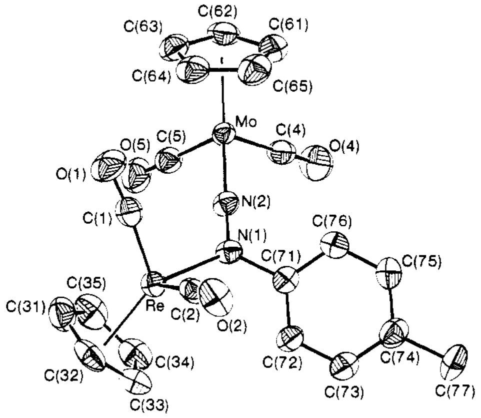

Figure 1. ORTEP diagram and atom-numbering scheme for a molecule of $(\eta^5\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}NNC_6H_4CH_3)Re(CO)_2(\eta^5\text{-}C_5H_5)$. Atoms are represented by 50% probability thermal ellipsoids.

The structure of compound **2** is composed of discrete molecules with no unusual intermolecular contacts. A perspective view of the molecule (Figure 1) illustrates the relative disposition of the carbonyl and Cp groups and the environment of the aryldiazenido ligand. The latter spans the metals in the form of a μ-N,N′ bridge of the type shown in structure C and acts as a 3-electron donor to Mo and a 2-electron donor to Re as shown in structure I. Consistent with this, the Mo–N(2) distance is 1.822 (4) Å, identical with the Mo–N distance (1.825 (4) Å) in $(HB(pz)_3)Mo(CO)_2(N_2Ph)$,[12] whereas the Re–N(1) length is 2.152 (4) Å. The Mo–N(2)–N(1) skeleton is essentially linear (178°) and the N(2)–N(1) distance is 1.256 (6) Å. This is marginally longer than the N–N distance in $(HB(pz)_3)Mo(CO)_2(N_2Ph)$ (1.211 (6) Å), but whether or not binding of the lone pair of electrons on N′ in **1** actually results in a lengthening of the N–N bond cannot be determined at this time without the structure of **1**

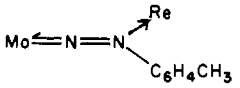

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Table III. Bond Parameters for $(\eta^5\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}NNC_6H_4CH_3)Re(CO)_2(\eta^5\text{-}C_5H_5)$

Distances (Å)

Re–CR(3)[a]	1.948	Mo–CR(6)[a]	2.021
Re–N(1)	2.151 (4)	Mo–N(2)	1.822 (4)
Re–C(1)	1.879 (6)	Mo–C(4)	1.994 (5)
Re–C(2)	1.873 (6)	Mo–C(5)	1.975 (6)
Re–C(31)	2.252 (6)	Mo–C(61)	2.338 (6)
Re–C(32)	2.259 (5)	Mo–C(62)	2.338 (6)
Re–C(33)	2.309 (6)	Mo–C(63)	2.350 (6)
Re–C(34)	2.314 (6)	Mo–C(64)	2.362 (6)
Re–C(35)	2.306 (6)	Mo–C(65)	2.365 (6)
N(1)–N(2)	1.256 (6)	C(31)–C(32)	1.419 (10)
N(1)–C(71)	1.468 (6)	C(32)–C(33)	1.436 (9)
C(71)–C(72)	1.378 (7)	C(33)–C(34)	1.379 (9)
C(72)–C(73)	1.380 (8)	C(34)–C(35)	1.422 (10)
C(73)–C(74)	1.393 (9)	C(35)–C(31)	1.398 (9)
C(74)–C(75)	1.375 (9)	C(61)–C(62)	1.406 (9)
C(74)–C(77)	1.522 (8)	C(62)–C(63)	1.417 (8)
C(75)–C(76)	1.381 (9)	C(63)–C(64)	1.405 (9)
C(76)–C(71)	1.362 (8)	C(64)–C(65)	1.429 (9)
C(1)–O(1)	1.165 (6)	C(65)–C(61)	1.402 (9)
C(2)–O(2)	1.166 (7)		
C(4)–O(4)	1.135 (7)		
C(5)–O(5)	1.137 (7)		

Angles (deg)

N(1)–Re–C(1)	93.2 (2)	N(2)–Mo–C(4)	96.0 (2)
N(1)–Re–C(2)	91.4 (2)	N(2)–Mo–C(5)	92.6 (2)
N(1)–Re–CR(3)[a]	124.5	N(2)–Mo–CR(6)[a]	129.9
C(1)–Re–C(2)	89.8 (2)	C(4)–Mo–C(5)	84.0 (2)
C(1)–Re–CR(3)[a]	123.6	C(4)–Mo–CR(6)[a]	118.4
C(2)–Re–CR(3)[a]	124.6	C(5)–Mo–CR(6)[a]	124.1
Re–N(1)–N(2)	118.9 (3)	C(31)–C(32)–C(33)	107.1 (5)
N(1)–N(2)–Mo	177.7 (4)	C(32)–C(33)–C(34)	107.4 (6)
Re–N(1)–C(71)	127.6 (3)	C(33)–C(34)–C(35)	109.8 (5)
N(2)–N(1)–C(71)	113.5 (4)	C(34)–C(35)–C(31)	107.0 (6)
N(1)–C(71)–C(72)	118.8 (5)	C(35)–C(31)–C(32)	108.7 (6)
N(1)–C(71)–C(76)	121.0 (5)	C(61)–C(62)–C(63)	108.5 (5)
C(72)–C(71)–C(76)	120.2 (5)	C(62)–C(63)–C(64)	107.2 (5)
C(71)–C(72)–C(73)	119.6 (5)	C(63)–C(64)–C(65)	108.6 (5)
C(72)–C(73)–C(74)	121.3 (5)	C(64)–C(65)–C(61)	107.2 (6)
C(73)–C(74)–C(75)	117.2 (5)	C(65)–C(61)–C(62)	108.6 (5)
C(73)–C(74)–C(77)	120.8 (6)	Re–C(1)–O(1)	173.8 (5)
C(75)–C(74)–C(77)	122.0 (6)	Re–C(2)–O(2)	176.1 (5)
C(74)–C(75)–C(76)	122.0 (6)	Mo–C(4)–O(4)	178.7 (5)
C(75)–C(76)–C(71)	119.6 (5)	Mo–C(5)–O(5)	178.9 (5)

[a] CR(3) and CR(6) refer to the centroids of the two cyclopentadienyl ligands.

for comparison. The geometry of N(1) is flat, as expected for approximate sp^2 hybridization, and the increase in coordination number due to the presence of the Re atom appears to decrease the N(2)–N(1)–aryl angle from typical values for singly bent N_2Ar ligands (which range from 118 to 136°, but are commonly near 120°)[14] to 113.5 (4)°.

There is a small but noticeable difference in the coordination of the two cyclopentadienyl groups. The group attached to molybdenum is symmetrically centered as shown by the insignificant difference in the extreme Mo–C distances (from 2.338 (6) to 2.365 (6) Å) and by the identical values of both the Mo–ring-centroid distance (Mo–CR(6) in Table III) and the Mo–ring-plane perpendicular distance (given in Table C in the supplementary data) at 2.021 Å. By comparison, the ring attached to Re is rather asymmetrically placed. Although this is not well revealed by comparing the Re–CR(3) distance (1.948 Å) and Re–ring-plane perpendicular distance (1.947 Å), there is an obvious trend and overall wider variation in the extreme Re–C(ring) distances, ranging from 2.252 (6) to 2.314 (6) Å.

The trend in these distances appears to be exactly that expected as a result of a difference in the trans influences of the ligand atoms located trans to the ring carbon atoms in question. One carbonyl group is situated roughly trans to C(33) and C(34) (C(1)–Re–C(33) = 150°; C(1)–Re–C(34) = 140°), while the other is situated trans to C(35) (C(2)–Re–C(35) = 156°). The larger trans influences of these CO groups result in Re–C(34) being the longest bond at 2.314 (6) Å followed closely by Re–C(33) and Re–C(35) at 2.309 (6) and 2.306 (6) Å, respectively. The Re–N(1) vector is placed (not quite symmetrically) trans to C(31) and C(32) (N(1)–Re–C(31) = 141°; N(1)–Re–C(32) = 150°). These Re–C distances are the shortest, at Re–C(31) = 2.252 (6) Å and Re–C(32) = 2.259 (5) Å, in accordance with the smaller trans influence of the Re–N(1) σ bond. In the case of the molybdenum-bound Cp ring, any differences that might exist in the relative trans influences of the σ- and π-bound carbonyl and aryldiazenido ligands appear insufficient to cause significant observable asymmetry in the Mo–ring distances.

A comparison of the IR and ^1H NMR parameters of the bimetallic complex **2** with those of the mononuclear molybdenum precursor **1** and $CpRe(CO)_2(THF)$ provides some evidence for the electronic changes that result from the substitution of THF by **1** in the formation of **2**. The two ν(CO) modes of **1** move up from 1991 and 1921 cm^{-1} to 2008 and 1945 cm^{-1} in **2**, and the Cp resonance moves downfield from δ 5.91 in **1** to δ 6.15 in **2**. Both effects are those expected as a result of withdrawal of electron density from the molybdenum atom in the process of N′ coordinating to the rhenium atom. Furthermore, N′ appears to be marginally a better donor to Re than is THF, since the ν(CO) positions in $CpRe(CO)_2(THF)$ at 1927 and 1859 cm^{-1} are lowered to 1920 and 1858 cm^{-1} in **2**; the Cp resonance is virtually unaffected, changing from δ 5.11 to δ 5.10 in **2**.

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Supplementary Material Available: Anisotropic thermal parameters (Table A), positional and thermal parameters for hydrogen atoms (Table B), data for mean-plane calculations (Table C), a complete table of interbond angles subtended at Mo and Re (Table D), and a listing of observed and calculated structure factors (Table E) (24 pages). Ordering information is given on any current masthead page.

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(14) A table of dimensions in singly bent N_2Ar ligands is given in ref 15.

(15) Barrientos-Penna, C. F.; Einstein, F. W. B.; Sutton, D.; Willis, A. C. *Inorg. Chem.* **1980**, *19*, 2740.