reaction is in fact not concerted over a wide range of leaving groups, the system might be useful for the study of leaving-group abilities or nucleofugalities,[24] which still appear to be poorly defined.[24-26]

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The other major finding of this work, which to our knowledge is novel, is that the elimination reaction is readily reversible with certain nucleophiles. This feature makes the system attractive for physical organic studies and also has implications, which we are pursuing, with respect to the β-lactam-processing enzymes.

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Nonplanar Amide Groups as Ligands

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Abstract: When the *trans*-osmium(IV) complexes Os(η^4-HBA-B)(PPh_3)$_2$, **1** (H_4HBA-B = 1,2-bis(2-hydroxybenzamido)benzene), and Os(η^4-CHBA-DCB)(PPh_3)$_2$, **2** (H_4CHBA-DCB = 1,2-bis(2-hydroxy-3,5-dichlorobenzamido)-4,5-dichlorobenzene), are treated with a strong π-acid ligand, carbon monoxide or *tert*-butyl isocyanide, a phosphine ligand is replaced and the substituted complexes are produced as the *cis*-α diastereomers Os(η^4-HBA-B)(CO)(PPh_3), **3**, and Os(η^4-CHBA-DCB)(*t*-BuNC)(PPh_3), **4**. X-ray crystal structure analyses show that **3** and **4** contain nonplanar amido ligands. The twisting about the C-N bond and the pyramidal distortions at the carbonyl-carbon and nitrogen atoms of the nonplanar amido groups are compared with all other reported cases of structured RC(O)NR'M and RC(OM')NR'M groups (R and R' are general groups but do not include H). The twist angles about the C-N bonds are significantly larger for **3** and **4** than have been observed previously. The effects of these deformations upon the bonding properties of the *N*-amido ligands are discussed.

The organic amide functional group, one of the most important building blocks in biological systems, is almost invariably found in a near-to-planar form. Rotational processes around the amide C-N bond disrupt amide delocalization and consequently are subject to substantial activation barriers (10-35 kcal·mol^{-1}).[2] Nonplanar amides have been recognized in formamide[3] and in some constrained molecules such as certain lactams[4,17] (including penicillin and cephalosporin antibiotics[5]), polycyclic spirodilactams,[6] and anti-Bredt bridgehead nitrogen compounds.[7] As part of a program aimed at developing new polyanionic chelating (PAC) ligands for highly oxidized and highly oxidizing complexes,[8-12] we have discovered a series of remarkable isomerization reactions in which planar N-coordinated organic amido groups are converted to distinctly nonplanar forms. The angular parameters of these unusual molecules are discussed in the context of all structurally characterized species containing RC(O)NR'M and RC(OM')NR'M fragments (R- and R'- are general groups but do not include H).

Experimental Section

Materials. Benzene (thiophene free, Aldrich), ethanol (U.S.I.), and hexanes (Aldrich) were reagent grade and were used as received. Dichloromethane (Baker) was distilled from calcium hydride (Aldrich) prior to use. *tert*-Butyl isocyanide (Alfa) and carbon monoxide (Matheson) were all used as received. Silica gel used in column chromatography was 60-200 mesh (Davison).

Physical Measurements. ^{1}H NMR spectra were recorded at 90 MHz on a Varian EM-390 spectrometer, at 89.83 MHz on a JEOL FX90-Q spectrometer, or at 500.135 MHz on a Bruker WM-500 spectrometer. ^{1}H chemical shifts are reported in ppm (δ) vs. Me_4Si with the solvent

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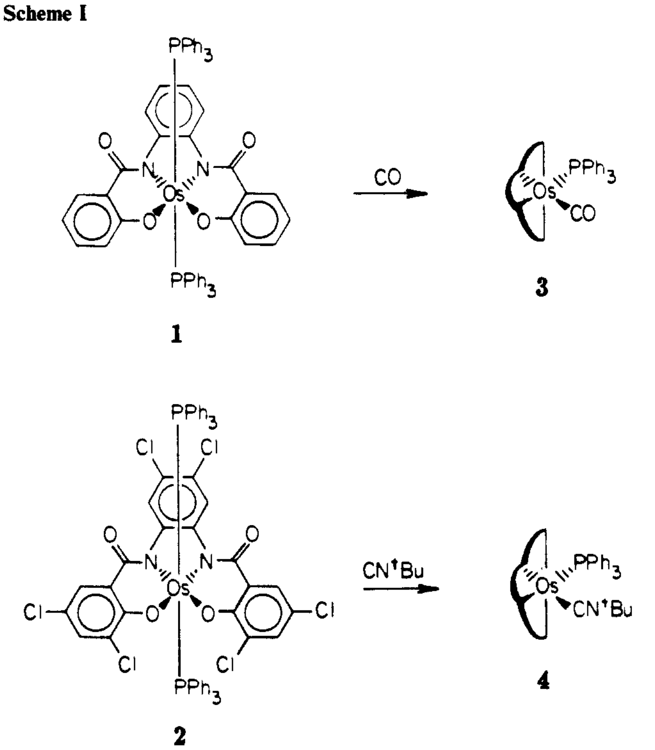
Table I. Summary of Crystal Data and Intensity Collection Information for *cis*-α-Os(η^4-HBA-B)(PPh_3)(CO) (3) and for *cis*-α-Os(η^4-CHBA-DCB)(PPh_3)(*t*-BuNC) (4)

compd	3	4
formula	$OsC_{39}H_{27}N_2O_5P$	$OsC_{43}H_{30}N_3Cl_6O_4P$
formula wt	824.83	1086.63
space group	$P2_1/c$	*Pbca*
a	18.007 (5) Å	22.09 (2) Å
b	10.848 (9) Å	19.92 (2) Å
c	17.848 (6) Å	19.40 (2) Å
α	90°	90°
β	106.85 (3)°	90°
γ	90°	90°
V	3337 (1) Å^3	8537 (4) Å^3
Z	4	8
λ	0.7107 Å	0.7107 Å
μ	2.389 mm^{-1}	3.45 mm^{-1}
D_{calcd}	1.642 g/mL	1.69 g/mL
scans	θ–2θ; 2.0° plus dispersn	ω; 1.0°
reflctns	4° < 2θ < 50°, $+h,\pm k,\pm l$	4° < 2θ < 30°, $\pm h,+k,+l$
bckgrnd time/scan time	0.5	1.0
colletd	11518 reflctns	3255 reflctns
avrgd	2146 reflctns	1706 reflctns
final no. of params	203	288
final cycle:		
R	0.059 (1868[a])	0.063 (1564[a])
$R_{3\sigma}$	0.044 (1512)	0.035 (1093)
S	2.62 (2146)	1.35 (1706)

[a] The number of reflections contributing to sums in parentheses.

Scheme I



(CDCl$_3$ δ 7.24 or CD$_2$Cl$_2$ δ 5.32) as internal standard. Infrared spectra were recorded on a Beckman IR 4240 spectrophotometer. Elemental analyses were obtained at the Caltech analytical facility. Solvents of crystallization were quantified by ^{1}H NMR spectroscopy of the authentic samples submitted for elemental analyses.

X-ray Data Collection and Structure Determination of 3. A crystal approximately 0.1 × 0.1 × 0.3 mm of Os(η^4-HBA-B)(PPh_3)(CO) was obtained from an ethanol/methylene chloride solution. Oscillation and Weissenberg photographs indicated a monoclinic space group, and the systematic absences (*h*0*l*, $l = 2n + 1$; 0*k*0, $k = 2n + 1$) verified the space group $P2_1/c$ (C^5_{2h}, no. 14). The intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromator and Mo Kα radiation (λ = 0.7107 Å). The unit cell parameters were obtained by least-squares refinement of the orientation matrix based on 25 reflections in the range: 15.0 < 2θ < 24.1°. The intensity measurements

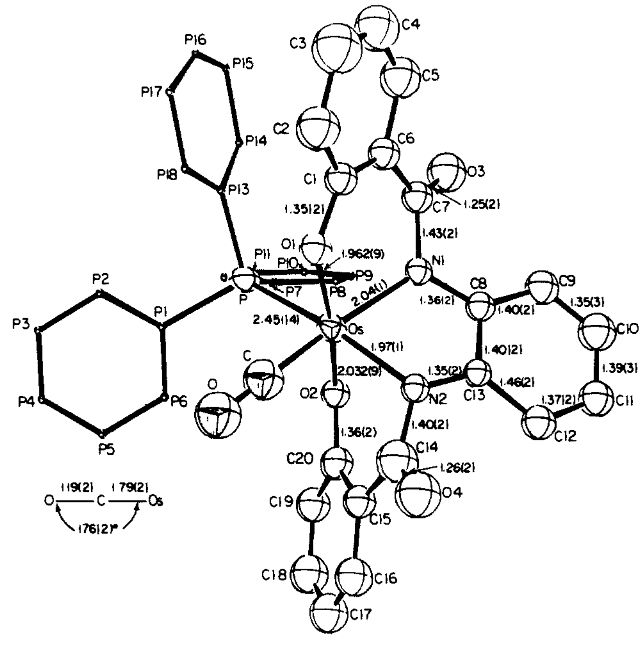


Figure 1. Molecular structure of 3.

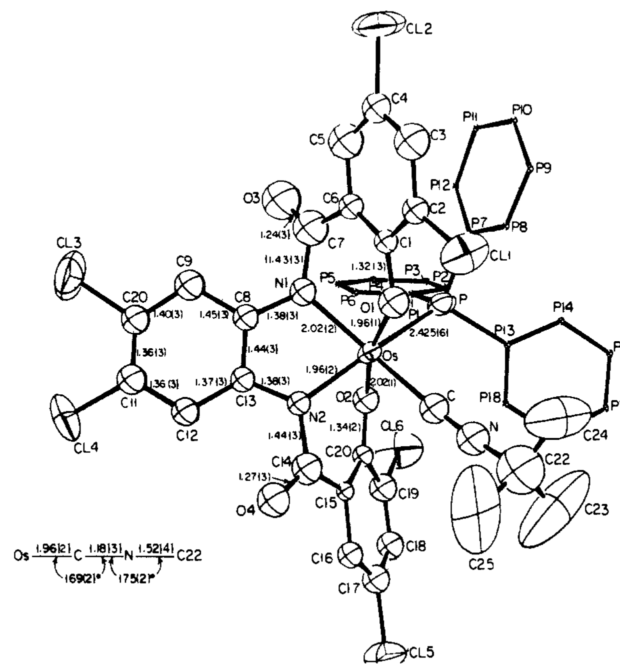


Figure 2. Molecular structure of 4.

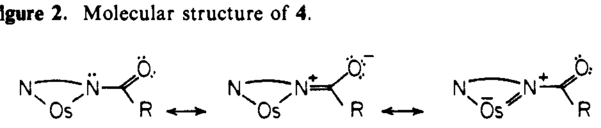


Figure 3. *N*-Amido ligand resonance structures.

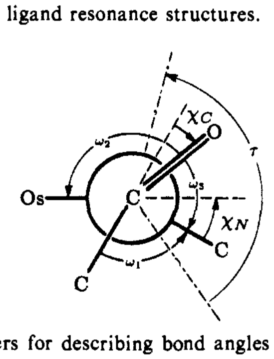


Figure 4. Parameters for describing bond angles in metallo-*N*-amido groups.

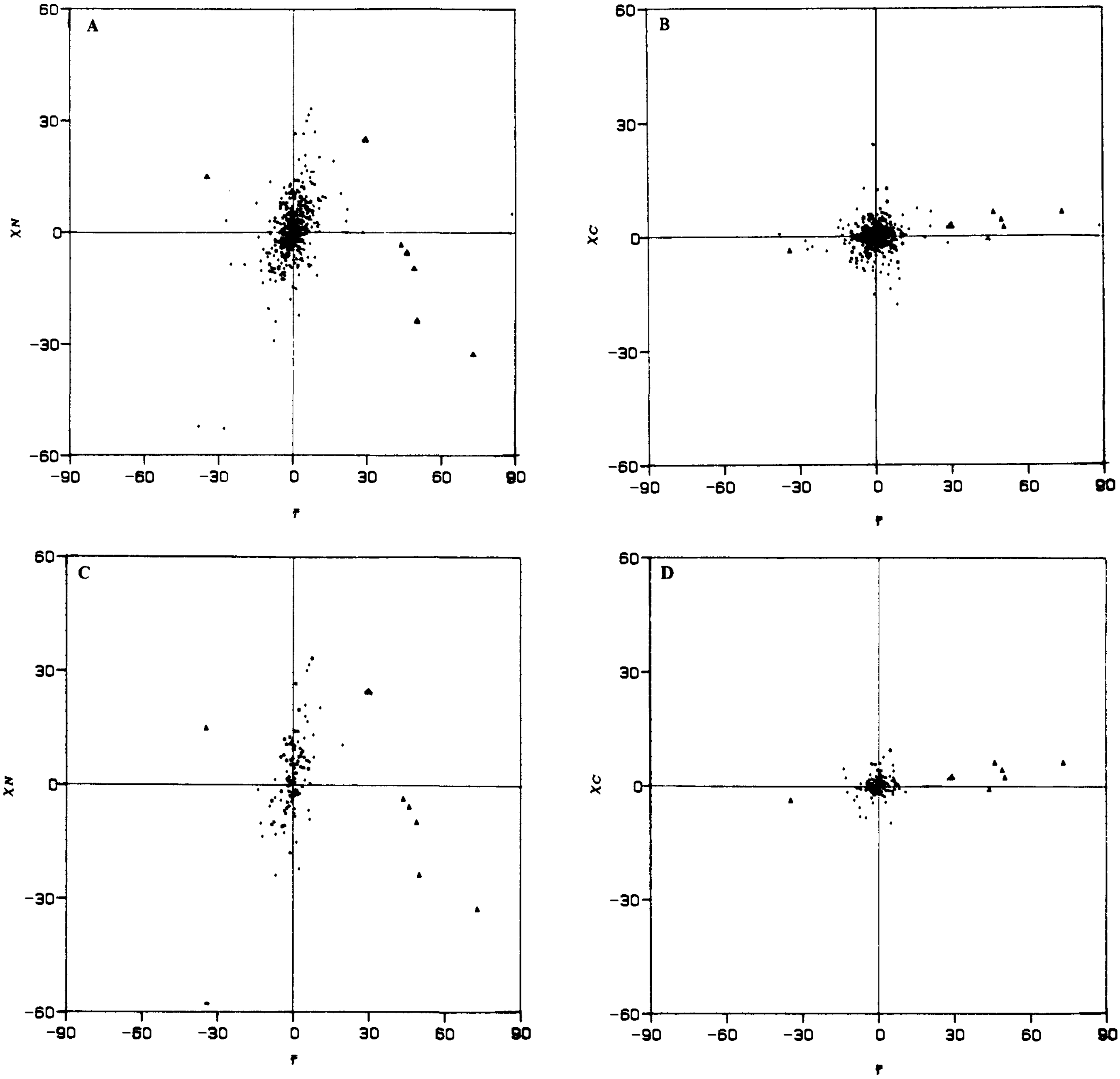


Figure 5. Angular parameters for metallo-N-amido and related fragments. (A) Plot of $\bar{\tau}$ vs. χ_N for all RC(O)NR′M and RC(OM′)NR′M fragments. (B) Plot of $\bar{\tau}$ vs. χ_C for all RC(O)NR′M and RC(OM′)NR′M fragments. (C) Plot of $\bar{\tau}$ vs. χ_N for RC(O)NR′M fragments where the RC(O)NR′H free base is a secondary amide. (D) Plot of $\bar{\tau}$ vs. χ_C for RC(O)NR′M fragments where the RC(O)NR′H free base is a second amide: ● literature points; ▲, points from this work and for osmium complexes of PAC ligands where large $\bar{\tau}$ values (>25°) are found.

were recorded for all reflections in one hemisphere ($4.0 < 2\theta < 50°$) using θ–2θ scans at a variable scan speed. The three check reflections indicated no decomposition, and the data were reduced to F_0^2; the variances of the intensities were obtained from counting statistics plus an additional term $(0.02 \times \text{scan counts})^2$. The form factors were taken from *The International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Those of osmium and phosphorus were corrected for anomalous dispersion. Details of the data collection are summarized in Table I.

The atomic position of the Os atom was derived from the Patterson map. Subsequent Fourier and difference maps revealed all non-hydrogen atoms of the ligands. After several cycles of least-squares refinement, hydrogen atoms were placed at a distance of 0.95 Å from their respective carbon atoms by assuming ideal geometry, with fixed $U = 0.065$ Å^2. Several cycles of full-matrix least-squares refinement minimizing $\Sigma w[F_0^2 - (F_c/k)^2]^2$ on all non-hydrogen atoms with anisotropic thermal parameters for Os and P and isotropic thermal parameters for all other atoms yielded $R_F = 0.059$, $R_{3_\sigma} = 0.044$, and GOF = 2.62; data-to-parameter ratio = 10.6.

X-ray Data Collection and Structure Determination of 4. A suitable crystal was obtained by slow crystallization from CH_2Cl_2/hexane. A series of oscillation and Weissenberg photographs indicated orthorhombic symmetry. Intensity data to $2\theta = 30°$ were collected on a locally-modified Syntex P2$_1$ diffractometer with graphite monochromator and Mo Kα radiation ($\lambda = 0.7107$ Å) using the w scans. Three check reflections, monitored after every 100 data measurements, indicated no decay for the first 3255 reflections ($\pm h,+k,+l$), but the intensity rapidly decreased thereafter; no further data was collected. The intensities were reduced to F_0's, and multiple observations were averaged to yield 1706 reflections. No absorption correction was applied. Details of the data collection are summarized in Table I.

The coordinates of the osmium atom were obtained from a three-dimensional Patterson function, and the remainder of the structure was determined from subsequent Fourier maps. Refinement was carried out by full-matrix least-squares, and the quantity minimized was $\Sigma w(\Delta^2)$ with $\Delta = F_0^2 - F_c^2$ and weight $w = 1/\sigma_{F_0^2}{}^2$. Form factors, with f′ added for osmium, phosphorus, and chlorine, were obtained from *The International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Calculations were carried out on a VAX 11/750 computer using the CRYM system.

Anisotropic Gaussian amplitudes were used for the osmium, phosphorus, chlorine, and methyl carbons atoms. The hydrogen atoms were fixed with $U = 0.20$ Å^2. Several cycles of least-squares refinements of

Table II. Selected Amide Torsional Angles and Calculated Nonplanarity Parameters for **3** and **4**

atoms	torsion	angle (deg)	parameter	value (deg)
		Compound **3**		
		(Amide Trans to CO)		
C_6–C_7–N_1–C_8	ω_{1a}	−128 (2)	χ_{Ca}	6 (2)
O_3–C_7–N_1–Os	ω_{2a}	−140 (1)	χ_{Na}	−6 (2)
O_3–C_7–N_1–C_8	ω_{3a}	46 (2)	$\bar{\tau}$	46 (2)
		(Amide Trans to PPh_3)		
C_{15}–C_{14}–N_2–C_{13}	ω_{1b}	−88 (2)	χ_{Cb}	6 (2)
O_4–C_{14}–N_2–Os	ω_{2b}	−127 (1)	χ_{Nb}	−33 (2)
O_4–C_{14}–N_2–C_{13}	ω_{3b}	86 (2)	$\bar{\tau}$	73 (2)
		Compound **4**		
		(Amide Trans to *t*-BuNC)		
C_6–C_7–N_1–C_8	ω_{1a}	−124 (2)	χ_{Ca}	4 (3)
O_3–C_7–N_1–Os	ω_{2a}	−138 (2)	χ_{Na}	−10 (2)
O_3–C_7–N_1–C_8	ω_{3a}	52 (3)	$\bar{\tau}$	49 (2)
		(Amide Trans to PPh_3)		
C_{15}–C_{14}–N_2–C_{13}	ω_{1b}	−117 (2)	χ_{Cb}	2 (3)
O_4–C_{14}–N_2–Os	ω_{2b}	−143 (2)	χ_{Nb}	−24 (2)
O_4–C_{14}–N_2–C_{13}	ω_{3b}	61 (3)	$\bar{\tau}$	50 (2)

the coordinates and thermal parameters of the non-hydrogen atoms yielded GOF = $[\Sigma w\Delta^2/(n-v)]^{1/2}$ = 1.35, n = 1706 reflections, v = 288 parameters, with $R_F = \Sigma|F_0 - |F_c||/\Sigma F_0$ = 0.063 ($I > 0$, 1564 reflections), and $R_{3\sigma}$ = 0.035 ($I \geq 3\sigma_I$, 1093 reflections).

Syntheses. All reactions were carried out in air unless otherwise noted. The compound *trans*-Os(η^4-CHBA-DCB)(PPh_3)$_2$, **2**, was prepared as described in the literature.[8] The preparation of *trans*-Os(η^4-HBA-B)(PPh_3)$_2$, **1**, will be described in a subsequent publication.[13]

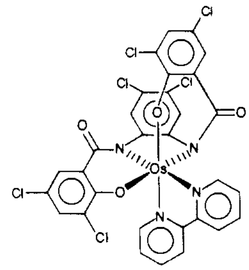
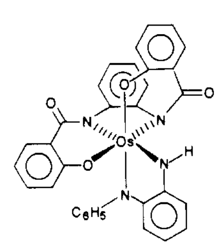
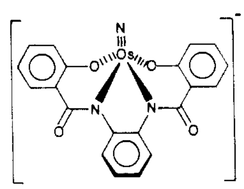
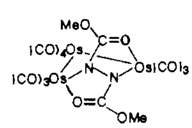
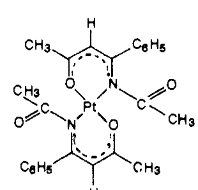
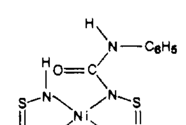
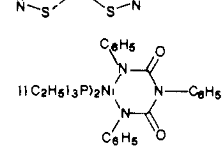
***cis*-α-Os(η^4-HBA-B)(PPh_3)(CO) (3).** Benzene (100 mL) was degassed with a nitrogen stream (20 min), *trans*-Os(η^4-HBA-B)(PPh_3)$_2$ (**1**) (500 mg, 0.472 mmol) was added, and carbon monoxide was then bubbled through the solution at room temperature (1.5 h). Methyl iodide (1 mL) was added, and CO addition was continued (0.5 h). Another portion of MeI (1 mL) was added, and CO addition was continued (0.5 h). The resulting violet solution was passed down a silica gel column by elution with a large quantity of benzene until the eluent was colorless. The benzene was removed on a rotary evaporator, and the residue was crystallized from CH_2Cl_2/ethanol to yield violet crystals: yield 125 mg (32%); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.01 (d, 1 H, ligand, J = 9 Hz), 8.23 (d, 1 H, ligand, J = 8 Hz), 8.01 (d, 1 H, ligand, J = 8 Hz), 7.66 (t, 1 H, ligand, J = 8 Hz), 7.40 (m, 3 H, phosphine H_p), 7.32 (under phosphine signal, 1 H, ligand), 7.30 (m, 12 H, phosphine $H_{o,m}$), 7.04 (t, 1 H, ligand, J = 7 Hz), 6.96 (t, 1 H, ligand, J = 8 Hz), 6.89 (t, 1 H, ligand, J = 8 Hz), 6.79 (t, 1 H, ligand, J = 8 Hz), 6.74 (d, 1 H, ligand, J = 8 Hz), 7.67 (t, 1 H, ligand, J = 8 Hz), 5.49 (d, 1 H, ligand, J = 8 Hz); IR (Nujol) 1695, 1637, 1595 ν_{CO}(nonplanar amides), 1985 cm^{-1} $\nu_{C\equiv O}$. Anal. Calcd for $C_{39}H_{27}N_2O_5OsP$: C, 56.79; H, 3.30; N, 3.40. Found: C, 56.59; H, 3.44; N, 3.38.

***cis*-α-Os(η^4-CHBA-DCB)(PPh_3)(*t*-BuNC) (4).** *trans*-Os(η^4-CHBA-DCB)(PPh_3)$_2$ (**2**) (20 mg, 0.016 mmol) and *tert*-butyl isocyanide were dissolved in benzene (10 mL) under nitrogen and heated under reflux (6 min) during which time the color changed from green to dark purple. The benzene was removed in vacuo, and the residue was recrystallized from CH_2Cl_2/hexane to give a dark crystalline product: yield 15 mg (85%); ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 8.22 (d, 1 H, phenol, J = 3 Hz), 7.27 (d, 1 H, phenol, J = 3 Hz), 7.87 (d, 1 H, phenol, J = 3 Hz), 7.06 (d, 1 H phenol, J = 3 Hz), 8.98 (s, 1 H, dichlorophenylene), 7.34 (s, 1 H, dichlorophenylene), 7.27 (dd, 6 H, phosphine H_o, $J_{o,p} \approx J_{o,m}$ = 8 Hz), 7.18 (dd, 6 H, phosphine H_m, $J_{m,p}$ = 7 Hz), 7.37 (t, 3 H, phosphine H_p), 1.35 (s, 9 H, *t*-Bu); IR (Nujol) 1650 ν_{CO} (nonplanar amides), 2160 cm^{-1} $\nu_{C\equiv N}$. Anal. Calcd for $C_{43}H_{30}Cl_6N_3O_4OsP$: C, 47.53; H, 2.78; N, 3.87. Found: C, 47.79; H, 2.99; N, 3.81.

Results and Discussion

The *trans*-bisphosphine osmium(IV) complexes **1** and **2** (see Scheme I) are valuable synthetic intermediates since the phosphines can be readily exchanged for many different ligands.[8] Exchange of one phosphine for a strong π-acid, carbon monoxide, or *tert*-butyl isocyanide occurs under mild conditions to afford the stable osmium(IV) complexes **3** and **4**.[13] Strong π-acid ligands, particularly carbon monoxide, are commonly found coordinated to basic metal centers, which for the later transition metals are usually confined to low oxidation state complexes.[14] The carbon monoxide CO stretching frequency in **3** is surprisingly low (1985 cm^{-1}). The existence of **3** and **4** further corroborates that the PAC ligands in these molecules are exceptional donors.[8,11,12] ^{1}H NMR data reveal that complexes **3** and **4** are no longer in the trans

Table III. Angular Parameters for RC(O)NR′M and RC(OM′)NR′M Fragments Where $\bar{\tau} > 25°$

compound	$\bar{\tau}$ (deg)	χ_N (deg)	χ_C (deg)	ref
 **5**	−35 1	15 5	−4 3	8
 **6**	22 44	6 −4	7 −1	16
 **7**	30 5	25 7	3 0	16
	−28 −38	−53 −52	−1 1	21 (cx)
	88	5	3	21 (xi)
	29	0	−2	21 (xxxvi)
	−27 −15	3 8	−3 3	21 (cvi)

(13) Carbon monoxide also reacts with **2** to give the **3** analogue. Keech, J. T., unpublished results. **1** reacts with *tert*-butyl isocyanide to give the **4** analogue. Anson, F. C.; Collins, T. J.; Gipson, S. L.; Keech, J. T.; Krafft, T. E.; Peake, G. T. *J. Am. Chem. Soc.*, in press.

form.[15] The planar PAC ligands in **1** and **2** (Scheme I) appeared to be relatively inflexible; it was of interest to learn which bond deformations would occur upon movement of the phenolate arms out of the equatorial plane to the axial sites. X-ray crystal structure analyses show that both molecules exist in the *cis-α* forms[15] (Figures 1 and 2, Table I).

Isomerization from trans to cis-α is achieved principally by rotation about the amide C–N bonds. The resulting amide geometries indicate an alteration of the amide bonding characteristics. The resonance structures for metallo-N-amido fragments are shown in Figure 3. The contribution from classical amide delocalization (structure B) should be attenuated upon isomerization to the cis-α isomer. A shift of the ν_{CO}(amide) IR bands to higher frequencies upon isomerization is consistent with this expectation (1605 cm^{-1} for **1** to 1637 and 1695 cm^{-1} for **3**, 1613 cm^{-1} for **2** to 1650 cm^{-1} for **4**). Apparently stabilization of the complex produced by the trans to cis-α isomerization is sufficient to compensate for the loss of amide delocalization.

Dunitz and Winkler and others in studies of amide group deformations defined two out-of-plane bending parameters, χ_N and χ_C (which describe trigonal planar to pyramidal distortions at the amide nitrogen and carbonyl carbon atoms), and a twist parameter, τ (which approximates the angle between the unperturbed nitrogen and carbonyl carbon pπ orbitals; Figure 4).[17,18] For a rigorously planar amide, both the nitrogen and carbonyl carbon atoms are sp^2 hybridized and χ_N and χ_C are both equal to 0°. However, the limiting value of τ can be either 0° or 180° depending upon whether the parent organic chain of the amide has the cisoid or transoid geometry, respectively. Carbon–nitrogen pπ overlap is expected to be close to zero when τ is ±90°. Here we define a modified version of τ, $\bar{\tau}$, such that

$$\bar{\tau} = (\tau) \bmod \pi$$

In contrast to τ this term does not distinguish cisoid and transoid geometries. However, $\bar{\tau}$ provides an approximate measure of the smaller angle between the unperturbed nitrogen and carbonyl carbon π orbitals and is easily visualized ($-90° \le \bar{\tau} \le 90°$). According to the measures, χ_C, χ_N, and $\bar{\tau}$, the N-amido ligands of **3** and **4** are decidedly nonplanar (Table II). A search of the Cambridge crystallographic database was undertaken for all structurally characterized RC(O)NR′M and RC(OM′)NR′M functionalities (R- and R′- are general groups but do not include H). Bibliographic references, coordinate data, and complete amide torsion analyses of these compounds were then compiled by utilizing the Cambridge database programs.[19] In Figure 5 the values of $\bar{\tau}$, χ_C, and χ_N for **3** and **4** are compared with those of all other reported RC(O)NR′M and RC(OM′)NR′M functionalities by plotting $\bar{\tau}$ vs. χ_N and $\bar{\tau}$ vs. χ_C (Figure 5).[8-12,16,20-22]

There are 457 data points in Figure 5 (parts A and B). Of these points 118 represent cases of monodentate N-amido ligands where the parent free base ligand is a secondary organic amide functional group. The secondary amide data are plotted separately in Figure

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5 (parts C and D). The large values of $\bar{\tau}$ (>25°) found for **3** and **4** are unprecedented for N-amido complexes which have the option to reduce $\bar{\tau}$ by isomerization at the metal center. It is important to note that these two molecules form a class of nonplanar N-amido complexes where the root cause of the nonplanarity appears to be added thermodynamic stabilization that results from the trans to cis-α isomerization. The *cis*-β-PAC ligand complexes **5**[8] and **6**[16] (Table III) apparently exhibit large $\bar{\tau}$ values because the structural constraints of the coordination sphere force the formation of nonplanar metallo-N-amido ligands. These molecules are inorganic analogues of the strained-ring organic amides and they form a second class of nonplanar metallo-N-amido complexes. Complex **7**[16] also shows an unusually high $\bar{\tau}$ value. It is likely that the nonplanarity is partly a result of distortions arising from the osmium atom sitting 0.55 Å out of the plane of the coordinated nitrogen and oxygen atoms. In the other four cases where the $\bar{\tau}$ values of RC(O)NR'M and RC(OM')NR'M groups are greater than 25° (Table III) either the N atom is involved in formal

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multiple bonding with its R′ ligand and/or the C(O) group is involved in multiple bonding with its R ligand (Table III).[22] None of the RC(O)NR′-ligands in these four cases are derived from parent organic amide functional groups.

Theoretical studies of amide group deformations[23] usually conclude that pyramidalization at nitrogen is energetically less demanding than pyramidalization at carbon or rotation about the C–N bond. It should be noted from Figure 5 that, in keeping with these studies, there is a much wider spread in χ_N values than in χ_C or $\bar{\tau}$ values. Amide nonplanarity has been considered previously for several metallo-N-amido groups which exhibit appreciable χ_N values.[20xxiv]

Complexes **3** and **4** are apparently the thermodynamically stable diastereomers as isomerization upon heating is not observed. The amide nitrogen lone pair, which in the planar amide ligand can be delocalized both onto the metal and the amide carbonyl group, is more available for π-donation to the metal in the nonplanar ligand. The amide nitrogen might also be expected to become a better σ-donor in the nonplanar form. In this context it is noteworthy that the geometries about the amide nitrogen atoms remain very close to trigonal planar when the amide is trans to the π-acceptor ligands suggesting that π-donation is present in these instances. The pyramidal distortions are larger for the amide ligands trans to phosphines (Table II). The ν_{CO}(amide) bands for **4** are found at the same wavenumber value, and the amido groups have almost identical $\bar{\tau}$ values, whereas the two amido ligands for **3** have different ν_{CO}(amide) bands and $\bar{\tau}$ values.

Metal–ligand bonding is probably greater with nonplanar N-amido ligands relative to the planar analogues. This conceivable increased bonding could be the principal compensating term to account for the substantial destabilization that is expected to accompany the loss of amide delocalization. We will present evidence in a subsequent paper to show that there is a significant increase in metal–ligand bonding for nonplanar N-amido ligands relative to planar N-amido ligands in these systems.

(22) The *cis*-diammineplatinum α-pyrrolidonato complex, $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_{5.48}\cdot 3H_2O$, which is an apparent mixture of two tetranuclear species of different oxidation levels, shows several abnormally large χ_C (21, 25, 26, 30, −36, 45, −45°, there are two distinct molecules per unit cell) and χ_N (35, −39, −48°) parameters which are difficult to rationalize. This structure contains other abnormal bond parameters. For instance, C–C single bond distances vary from 1.36–1.90 Å. The points derived from this work by Matsumoto, Takahashi, and Fuwa are not included in Figure 5 (Matsumoto, K.; Takahashi, H.; Fuwa, K. *J. Am. Chem. Soc.* **1984**, *106*, 2049–2054). The related pyrrolidinato, mixed-valence, tetranuclear species, $[Pt_4(NH_3)_8(C_6H_6NO)_4](NO_3)_6\cdot H_2O$, has been the subject of two reports by Matsumoto and Fuwa and Matsumoto, Takahashi, and Fuwa, Matsumoto, K.; Fuwa, K. *J. Am. Chem. Soc.* **1982**, *104*, 897–898, Matsumoto, K.; Takahashi, H.; Fuwa, K. *Inorg. Chem.* **1983**, *22*, 4086–4090). In the former a trihydrate is claimed for which several χ_C values (−24, 39°) are extremely large. In the latter a dihydrate is claimed where one χ_C value is unreasonable (−74°), and another is at least inexplicably large (−28°). Presumably some atomic coordinates are inaccurate. The authors noted difficulties with this determination. The points for these structures are also excluded from Figure 5.

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Supplementary Material Available: Listing of atomic coordinates, Gaussian amplitudes, bond lengths and angles, listings of structure factor tables, and complete listing of referenced compounds and torsion angle determinations (106 pages). Ordering information is given on any current masthead page.

Communications to the Editor

Demonstration of Heteroaromaticity via d-Orbital Overlap in a Cyclic Conjugated Sulfone: NMR, Crystallography, and ab Initio Calculation[1]

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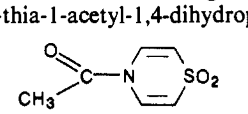
Questions regarding the nature of the interaction between second-row elements such as sulfur and carbon π-electron systems, including the relative merits of p(C)–d(S) vs. p(C)–p(S) overlap, have been the subject of extensive investigation and sometimes heated controversy.[3,4]

In this paper we exploit the extreme sensitivity of electronic energy of cyclic π-electron species to the number of π electrons associated with the ring in order to assess the possible existence and magnitude of sulfur π-system overlap.

The system we have chosen to investigate is the sulfone heterocycle 4,4-dioxy-4-thia-1-acetyl-1,4-dihydropyridine (**1**).[5,6] We



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shall show how a combination of NMR line-shape analysis, X-ray crystallography, and ab initio calculations implicates p–d bonding unequivocally and for the first time.

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