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Comparison of Isoelectronic Cyclopentadienyl, Indenyl, and Hydrotris(3,5-dimethylpyrazolyl)borate Complexes of Osmium(VI)

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Osmium(VI) complexes with cyclopentadienyl, indenyl, and hydrotris(3,5-dimethylpyrazolyl)borate ligands result from the reaction between $[Os(N)Ph_2(py)_2][BF_4]$ and sodium cyclopentadienide, potassium indenide, or potassium hydrotris(3,5-dimethylpyrazolyl)borate. The molecular structures of the resulting complexes, $CpOs(N)Ph_2$ (**1**), $InOs(N)Ph_2$ (**2**), and $Tp^*Os(N)Ph_2$ (**3**), have been determined by X-ray diffraction analysis. The cyclopentadienyl-type ligand in each complex is distorted due to the strong trans effect of the nitrido group.

Introduction

Since its introduction into transition metal chemistry in the early 1950s, the cyclopentadienyl (Cp) ligand has played a prominent role in organotransition metal research.[1] It can coordinate metals in η^5, η^3, or η^1 bonding modes but η^5-cyclopentadienyl complexes are by far the most common. The interconversion of the possible bonding modes of the cyclopentadienyl ligand changes the total electron count of the complex and may be important in catalytic reactions involving metal−cyclopentadienyl complexes.[2] The ability of the cyclopentadienyl ligand to "slip" from a higher to a lower bonding mode removes an electron pair from the metal center and creates a vacant low-energy metal orbital for nucleophilic attack.

The presence of an isoelectronic indenyl (In) ligand has an even more pronounced effect on the reaction rate and mechanism of a metal complex. Mawby and Hart-Davis found that complexes containing an indenyl ligand had reaction rates 10−20 times faster than the corresponding cyclopentadienyl systems.[3] Basolo and co-workers reported an indenyl system that shows a 10^8 times increase in rate over the analogous cyclopentadienyl system and coined the term "indenyl ligand effect" to describe this rate enhancement.[4] The increase in rate over the cyclopentadienyl systems may be due to the ability of the indenyl ligand to stabilize the allyl−ene intermediate formed when the ring slips from η^5 to η^3 by aromatization of the C_6 ring. Like cyclopentadienyl ligands, indenyl ligands can bind to metals in an η^5, η^3, or η^1 mode. The η^5-indenyl complexes are most common.

Poly(pyrazolyl)borates were first introduced by Trofimenko in 1966.[5] The parent hydrotris(pyrazolyl)borate (Tp) and its alkyl-substituted analogs such as hydrotris(3,5-dimethylpyrazolyl)borate (Tp*) are the most common.[6] Like the indenyl ligand, tris(pyrazolyl)borates are isoelectronic to cyclopentadienyl ligands. The tris(pyrazolyl)borates differ from cyclopentadienyl and indenyl ligands in that they bind in a σ rather than a π fashion to the metal center. Nevertheless, the derivative chemistry of the tris(pyrazolyl)borates is quite similar to that of cyclopentadienyl ligands. Tris(pyrazolyl)borate complexes tend to be more stable than their cyclopentadienyl analogs.[7] In fact, the presence of hydrotris(pyrazolyl)borate, hydrotris(3,5-dimethylpyrazolyl)borate, and other bulkier alkyl-substituted analogs stabilize otherwise unattainable structures such as L*CuCO (L* = Tp or Tp*).[8] This stabilization is due, at least in part, to the ability of the substituent in the 3-position of the pyrazolyl ring to sterically protect the metal center. This is not surprising considering the difference in cone angles between cyclopentadienyl (100°) and hydrotris(pyrazolyl)borate (199°).[9] The presence of substituents other than hydrogen in the 3-position further increases the cone angle, for example hydrotris(3,5-dimethylpyrazolyl)borate has a cone angle of 236°.[9b] Several studies have suggested that hydrotris(pyrazolyl)borate is closer in its electron-donor properties to pentamethylcyclopentadienyl (Cp*) than to cyclopentadienyl.[10] We have not found studies comparing the structure and properties of of indenyl and tris(pyrazolyl)borate or tris(3,5-dimethylpyrazolyl)borate complexes in the literature.

We previously reported the syntheses of the osmium alkyl complexes $(C_5R_5)Os(N)(CH_2SiMe_3)_2$ (R = H, Me) and $CpOs(N)(Me)_2$.[11] These nitrido complexes are thermally stable and stable to air and water. Because they are coordinatively saturated, 18-electron complexes,

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[1] (a) Kealy, T. J.; Paulson, P. L. *Nature (London)* **1951**, *168*, 1039−1040. (b) Miller, S. A.; Tebboth, J. A.; Tremaine, J. F. *J. Chem. Soc.* **1952**, 632−635. (c) Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 2125−2126.

[2] O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307−318.

[3] Hart-Davis, A. J.; Mawby, R. J. *J. Chem. Soc. A* **1969**, 2403−2407.

[4] (a) Ji, L.; Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740−745. (b) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908−5912.

[5] Trofimenko, S. *J. Am. Chem. Soc.* **1966**, *88*, 1842−1844.

[6] (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980. (b) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115−209.

[7] Trofimenko, S. *Acc. Chem. Res.* **1979**, *4*, 17−22.

[8] Niedenzu, K.; Trofimenko, S. *Top. Curr. Chem.* **1986**, *131*, 1−37.

[9] (a) Frauendorfer, E.; Brunner, H. *J. Organomet. Chem.* **1982**, *240*, 371. (b) Rheingold, A. L.; Ostrander, R. L.; Haggerty, B. S.; Trofimenko, S. *Inorg. Chem.* **1994**, *33*, 3666−3676.

[10] (a) Sharp, P. R.; Bard, A. J. *Inorg. Chem.* **1983**, *22*, 2689−2693.

[11] (a) Marshman, R. W.; Shusta, J. M.; Wilson, S. R.; Shapley, P. A. *Organometallics* **1991**, *10*, 1671−1676. (b) Shusta, J. Ph.D. Thesis, University of Illinois, Urbana, IL, 1992.

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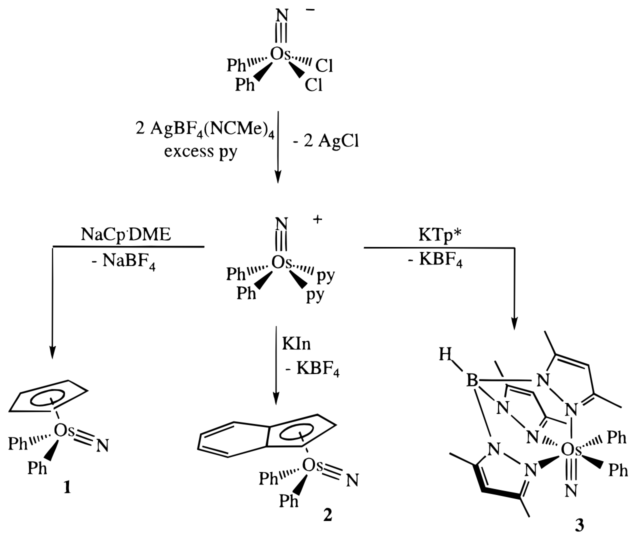
Scheme 1



they do not react with donor molecules. The nitrogen atom in $CpOs(N)(CH_2SiMe_3)_2$ behaves as a Lewis base and forms adducts with boron trifluoride and silver(I).[11a] The cationic methyl imido analogues of $(C_5R_5)Os(N)(CH_2SiMe_3)_2$ (R = H, Me) and $CpOs(N)(Me)_2$ result from their reactions with excess methyl trifluoromethanesulfonate.[11] The imido group in $[CpOs(NCH_3)(CH_2SiMe_3)][SO_3CF_3]$ reacts with bases and with unsaturated organic molecules.[12]

Because the nature of the ancillary ligands may dramatically affect the imido-group transfer reaction, we are engaged in a study of related nitrido and imido complexes with different alkyl and aryl ligands and with different Cp-type ligands. In this paper, we discuss the syntheses, molecular structure, and characteristics of a series of diaryl nitrido complexes of osmium(VI) containing cyclopentadienyl, indenyl, and hydrotris(3,5-dimethylpyrazolyl)borate ligands.

Results

Syntheses of $CpOs(N)Ph_2$, $InOs(N)Ph_2$, and $Tp^*Os(N)Ph_2$. The addition of 2 equiv of $AgBF_4(NCMe)_4$ to either $[PPh_4][Os(N)Ph_2Cl_2]$ or $[N(n\text{-}Bu)_4][Os(N)Ph_2Cl_2]$ in the presence of pyridine presumably forms a pyridine-containing intermediate $[Os(N)Ph_2(py)_2][BF_4]$ (Scheme 1). This complex was not characterized, but the (trimethylsilyl)methyl, $[M(N)(CH_2SiMe_3)_2(py)_2][BF_4]$ (M = Os, Ru), and the methyl analog, $[Ru(N)(Me)_2(py)_2][BF_4]$, were prepared in this manner and have been fully characterized.[11b,13] The reaction between $[Os(N)Ph_2(py)_2][BF_4]$ and NaCp·DME in tetrahydrofuran produced the cyclopentadienyl complex, $CpOs(N)Ph_2$, **1**, in an 18% isolated yield. Similarly, the addition of [K][In] to a tetrahydrofuran solution of $[Os(N)Ph_2(py)_2][BF_4]$ produced $InOs(N)Ph_2$, **2**, in 32% isolated yield. The hydrotris(3,5-dimethylpyrazolyl)borate complex, Tp^*OsNPh_2, **3**, was prepared in 28% isolated yield by addition of [K][Tp*] to a tetrahydrofuran solution of $[Os(N)Ph_2(py)_2][BF_4]$. The cyclopentadienyl and indenyl complexes are orange crystalline solids, while the hydrotris(3,5-dimethylpyrazolyl)borate complex is a deep red crystalline material. All three complexes were soluble in organic solvents.

Spectroscopic Properties. Each of the diphenyl nitrido osmium(VI) complexes (**1**–**3**) was characterized by IR and ^1H and ^{13}C NMR spectroscopies and elemental analysis. We assigned the osmium–nitrogen stretching vibrations in the IR spectra of these complexes (**1**, 1080 cm^{-1}; **2**, 1092 cm^{-1}; **3**, 1094 cm^{-1}) by comparison to the bands of known compounds. Osmium–nitrogen stretching frequencies fall in the range of 1008–1130 cm^{-1}.[14] For example, the υ_{Os-N} for $[N(n\text{-}Bu)_4][OsNPh_4]$ is at 1123 cm^{-1} and that for $[N(n\text{-}Bu)_4][OsNPh_2Cl_2]$ is at 1130 cm^{-1}.[15] The band at 1094 cm^{-1} in **3** shifts to 1057 cm^{-1} in the ^{15}N-labeled complex, $Tp^*Os^{15}NPh_2$. This is close to the predicted value of 1061 cm^{-1} based on a simple harmonic oscillator model and confirms our assignment.[16]

The ^1H NMR spectrum of **1** contains resonances for the phenyl protons at δ 7.45 and 7.04 in a 4:6 ratio and a singlet for the five equivalent protons of the cyclopentadienyl ligand at δ 5.95 in CD_2Cl_2. The $^{13}C\{^1H\}$ NMR spectrum shows one peak at δ 97.30 for the equivalent carbons of the cyclopentadienyl ligand and four resonances, as expected, for the two equivalent phenyl ligands.

Unfortunately, the ^1H NMR spectrum of **2** is not very revealing due to the significant overlap of the phenyl and indenyl proton resonances. The $^{13}C\{^1H\}$ NMR spectrum is easier to interpret. It contains nine resonances for the carbons of the phenyl and indenyl ligands, consistent with a solution structure in which a mirror plane bisects the indenyl ligand and the two freely rotating phenyl ligands. The ^{13}C chemical shift of the carbons at the ring juncture correlates with the degree of distortion in η-C_9H_7 complexes.[17] Baker and Tulip calculate the chemical shift difference, $\Delta\delta(C) = \delta(C(\eta\text{-indenyl})) - \delta(C(\text{indenyl sodium}))$, and relate this value to the hapticity of the indenyl ligand.[17b] The $\Delta\delta(C)$ of -1.3 for **2** predicts that the indenyl group is between a distorted η^5-In and η^3-In ligand.

The ^1H NMR spectrum of **3** shows peaks in a 6:3:6:3 ratio for the pyrazolyl methyl protons and peaks in a 2:1 ratio for the methine protons on the pyrazolyl ring, suggesting that the coordinated hydrotris(3,5-dimethylpyrazolyl)borate ligand is bisected by a mirror plane. Five resonances in the phenyl region show that the equivalent phenyl groups are not freely rotating. The $^{13}C\{^1H\}$ NMR data is also consistent with a structure having two equivalent but not freely rotating phenyl ligands.

Molecular Structure. The molecular structures of **1**–**3** were confirmed by single-crystal X-ray diffraction. Significant bond distances and angles for each structure are shown in Table 1. SHELXTL plots of each are shown in Figures 1, 2, and 3.

For all three complexes the osmium–nitrogen bond distances for the nitrido ligand fall within the expected range (1.58–1.68 Å) for osmium–nitrogen triple bonds.[14]

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[12] Shapley, P. A.; Shusta, J. M.; Hunt, J. L. *Organometallics* **1996**, *15*, 1622–1629.

[13] 3. Shapley, P. A.; Schwab, J. J.; Wilson, S. R. *J. Coord. Chem.* **1994**, *32*, 213–232.

[14] Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple bonds*; John Wiley & Sons: New York, 1988.

[15] Allen, J. L. Ph.D. Thesis, University of Illinois at Urbana-Champaign, Urbana, IL, 1996.

[16] Marshman, R. W. Ph.D. Thesis, University of Illinois at Urbana-Champaign, Urbana, IL, 1990.

[17] (a) Kohler, F. H. *Chem. Ber.* **1974**, *107*, 570–574. (b) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839–845.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 1, 2, and 3

bond distances (Å)		bond angles (deg)	
	Compound **1**		
Os(1)–N(1)	1.660(9)	N(1)–Os(1)–C(6)	97.2(5)
Os(1)–C(1)	2.234(12)	N(1)–Os(1)–C(12)	95.8(4)
Os(1)–C(2)	2.190(11)	C(6)–Os(1)–C(12)	88.7(4)
Os(1)–C(3)	2.278(11)	C(6)–Os(1)–C(4)	80.7(4)
Os(1)–C(4)	2.514(11)	C(12)–Os(1)–C(5)	84.0(4)
Os(1)–C(5)	2.506(11)	N(1)–Os(1)–C(2)	108.9(5)
Os(1)–C(6)	2.109(11)		
Os(1)–C(12)	2.110(11)		
	Compound **2**		
Os(1)–N(1)	1.632(4)	N(1)–Os(1)–C(1)	96.0(2)
Os(1)–C(13)	2.668(5)	N(1)–Os(1)–C(7)	100.9(2)
Os(1)–C(18)	2.687(5)	C(1)–Os(1)–C(7)	85.6(2)
Os(1)–C(19)	2.294(5)	C(1)–Os(1)–C(21)	94.7(2)
Os(1)–C(20)	2.190(5)	C(7)–Os(1)–C(19)	94.0(2)
Os(1)–C(21)	2.259(5)	N(1)–Os(1)–C(20)	130.9(2)
Os(1)–C(1)	2.108(4)		
Os(1)–C(7)	2.088(4)		
	Compound **3**		
Os(1)–N(1)	1.648(3)	N(1)–Os(1)–C(1)	95.70(14)
Os(1)–N(2)	2.139(3)	N(1)–Os(1)–C(7)	95.37(14)
Os(1)–N(4)	2.164(3)	C(1)–Os(1)–C(7)	94.29(13)
Os(1)–N(6)	2.352(3)	N(1)–Os(1)–N(2)	101.30(13)
Os(1)–C(1)	2.119(3)	N(1)–Os(1)–N(4)	97.72(13)
Os(1)–C(7)	2.119(3)	N(1)–Os(1)–N(6)	178.02(12)
N(3)–B(1)	1.558(5)	N(2)–Os(1)–N(4)	84.99(10)
N(5)–B(1)	1.552(5)	N(2)–Os(1)–N(6)	80.47(10)
N(7)–B(1)	1.535(5)	N(4)–Os(1)–N(6)	81.51(10)
N(2)–N(3)	1.375(4)	C(1)–Os(1)–N(4)	90.05(12)
N(4)–N(5)	1.373(4)	C(1)–Os(1)–N(6)	82.49(11)
N(6)–N(7)	1.382(4)	C(7)–Os(1)–N(2)	86.90(12)
		C(7)–Os(1)–N(6)	85.59(11)

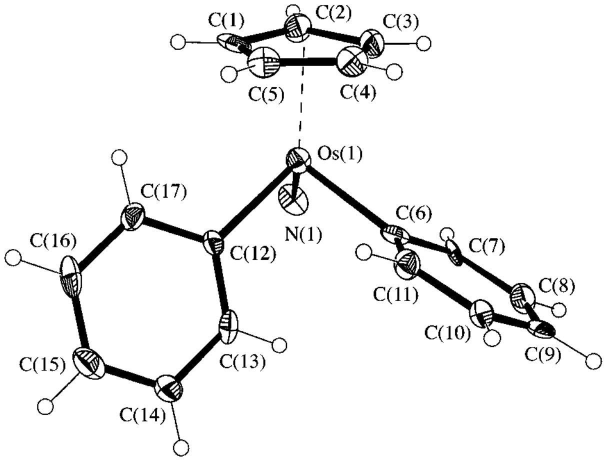

Figure 1. SHELXTL plot of **1** showing 35% probability ellipsoids for non-H atoms and circles of arbitrary size for H atoms.

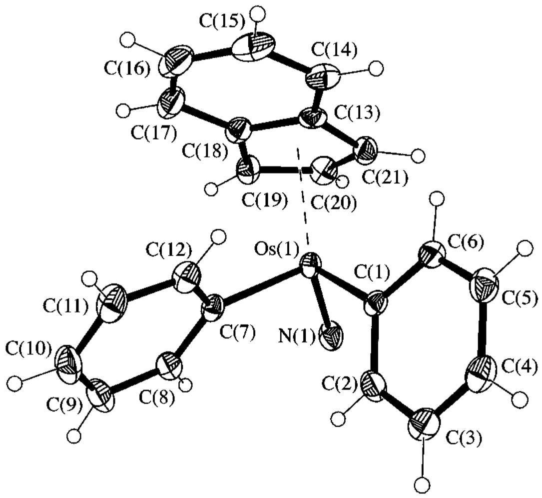

Figure 2. SHELXTL plot of **2** showing 35% probability ellipsoids for non-H atoms and circles of arbitrary size for H atoms.

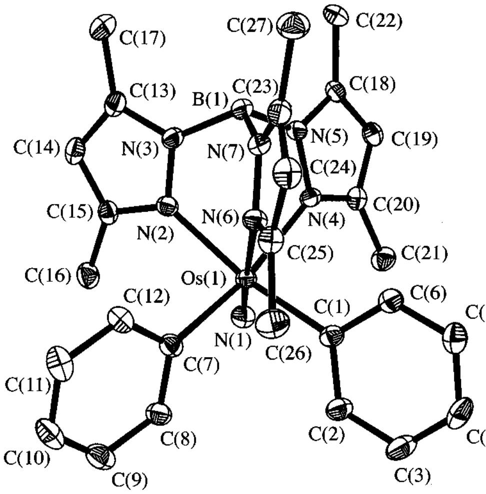

Figure 3. SHELXTL plot of **3** showing 35% probability ellipsoids for non-H atoms. H atoms have been left out for clarity.

The osmium centers in both **1** and **2** are in a distorted pseudooctahedral three-legged piano-stool environment. The phenyl ligands in both complexes are bent away from the nitrido group with N–Os–C(*ipso*) angles of more than 95°. In addition, both the cyclopentadienyl and indenyl ligands in **1** and **2** exhibit significant slip distortions from η^5 toward η^3 coordination. Hinge and fold angles (HA and FA) which represent the bending of the indenyl ligand at C19/C21 and C13/C18, respectively, as well as the slip value (Δ_{M-C}), are commonly used in measuring the degree of hapticity distortions in indenyl complexes; similarly, HA and Δ_{M-C} values can also be calculated for cyclopentadienyl complexes.[18] In complex **1**, HA = 5.6° and Δ_{M-C} = 0.25 Å, and in complex **2**, HA = 13.5°, FA = 14.3°, and Δ_{M-C} = 0.40 Å. In both **1** and **2**, it is the two carbons of the five-membered ring which are *trans* to the nitride that are significantly further away from the metal than the others. In addition, the structure of **2** is consistent with the prediction made by Crabtree and co-workers that for indenyl complexes the predominant conformation places the six-membered ring of the indenyl ligand *trans* to the ligand or ligands with the greatest *trans* effect.[19]

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(18) HA is the angle between normals to least-squares planes defined by C1, C2 C3 and C1, C3, C4, and C5 for **1** and planes defined by C19, C20, and C21 and C13, C18, C19, and C21 for **2**; FA is the angle between normals to least square planes defined by C19, C20, and C21 and C13, C14, C15, C16, C17, and C18 for **2**; Δ_{M-C} is [M–C$_{av}$(for C4,C5)]–[M–C$_{av}$(for C1,C3)] for **1** and [M–C$_{av}$ (for C13,C18)]–[M–C$_{av}$ (for C19,C21)] for **2**; the following references use similar parameters for determining slip distortions, see: (a) Marder, T. B.; Calabrese, J. C.; Roe, D. C.; Tulip, T. H. *Organometallics* **1987**, *6*, 2012–2014. (b) Carl, R. T.; Hughes, R. P.; Rheingold, A. L.; Marder, T. B.; Taylor, N. J. *Organometallics* **1988**, *7*, 1613–1624. (c) Kakkar, A. K.; Jones, S. F.; Taylor, N. J.; Collins, S.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 1454–1456. (d) Westcott, S. A.; Kakker, A. K.; Stringer, G.; Taylor, N. J.; Marder, T. B. *J. Organomet. Chem.* **1990**, *394*, 777–794. (e) Huber, T. A.; Bélanger-Gariépy, F.; Zargarian, D. *Organometallics* **1995**, *14*, 4997–4999. (f) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreno, E. *Organometallics* **1996**, *15*, 2137–2147.

(19) Faller, J. W.; Crabtree, R. H.; Habib, A. *Organometallics* **1985**, *4*, 929–935.

The osmium center in **3** is in a distorted octahedral environment. The three N−Os−N angles of the TpOs fragment are all less than 90°, as expected due to the chelating nature of the hydrotris(3,5-dimethylpyrazolyl)borate ligand, while the C(1)−Os(1)−C(7) angle is 94.29(13)°. The four ligands *cis* to the nitrido group are all bent away from this ligand so that the osmium is shifted out of the least-squares plane defined by C(1), C(7), N(2), and N(4) by 0.276(2) Å. In addition, the two chelating pyrazole rings *trans* to the phenyl rings are approximately 0.2 Å closer to the osmium than the third, which is *trans* to the nitride. A similar trend was observed in an analogous alkylidene complex Os(C-*t*-Bu)(CH_2-*t*-Bu)$_2$(Tp).[20] In this case, the Os−N distances for the pyrazolyl nitrogens *trans* to the two neopentyl groups are around 0.1 Å shorter than that for the pyrazolyl nitrogen *trans* to the neopentylidyne. This behavior is expected based on the *trans* influence of both the nitrido and the alkylidyne ligands.

Discussion

On the basis of the NMR and X-ray data, the structures of **2** and **3** are similar in the solution and solid states. The NMR data suggest that at room temperature in the solution state the phenyl ligands of **2** rotate freely while in **3** free rotation is blocked by the bulky hydrotris(3,5-dimethylpyrazolyl)borate ligand. The NMR data also indicates that the phenyl ligands in **1** rotate freely. However, there appears to be a slight difference in the solution and solid state structures for **1**. Because the single-crystal X-ray structure shows a significant distortion of the Cp ligand toward an η^3-bonding mode in the solid state, a dynamic process must occur in solution at room temperature to equilibrate the carbons and protons of the cyclopentadienyl ligand. Unfortunately, all resonances broaden in the ^{1}H NMR spectrum at −90 °C. This is probably due to the decreased solubility of the compound under these conditions.

The values of HA and Δ_{M-C} which are calculated from single-crystal X-ray diffraction data are useful in determining the degree of hapticity distortions in cyclopentadienyl and indenyl complexes. In general, for η^5-Cp complexes, values for HA are less than 5° and values for Δ_{M-C} are less than 0.15 Å.[19] In contrast, the few structurally characterized η^3-Cp complexes have values for HA closer to 20° and Δ_{M-C} values around 0.6 Å.[21] Using these criteria, **1** (HA = 5.6°; $\Delta_{M-C} = 0.25$ Å) has a distorted η^5-cyclopentadienyl ligand. A few other complexes have a similar distortion. Pentamethylcyclopentadienylrhenium complexes investigated by Herrmann and co-workers including Cp*Re(O)(Me)(CH_2CMe_3)[22] (HA = 7.5°; $\Delta_{M-C} = 0.227$ Å), Cp*Re(N-*t*-Bu)Cl_2[23] (HA = 8.3°; $\Delta_{M-C} = 0.244$ Å), Cp*ReOCl_2[23,24] (HA = 9.3°; $\Delta_{M-C} = 0.251$ Å), Cp*ReOMe_2[24] ($\Delta_{M-C} = 0.264$ Å), and Cp*ReO($CH_2C_6H_5$)$_2$[24] ($\Delta_{M-C} = 0.259$ Å) show significant slip distortions of this type. The silver adduct of the trimethylsilylmethyl analog {[CpOs(μ-N)(CH_2SiMe_3)$_2$]$_2$Ag}BF_4 has two distinct and only slightly distorted cyclopentadienyl ligands (HA = 4.3°, 2.1°; $\Delta_{M-C} = 0.19$, 0.16 Å).[11a]

In general, indenyl complexes considered to be η^5 have values of HA less than 10° and values of Δ_{M-C} less than 0.25 Å,[19] in contrast to those considered to be η^3 which have values of HA between 20° and 30° and values of Δ_{M-C} between 0.69 and 0.80 Å.[18c] The indenyl ligand in **2** (HA = 13.5°; FA = 14.3°; $\Delta_{M-C} = 0.40$ Å) falls between the ranges normally observed for η^3 and η^5 complexes, but the distortion in **2** is more pronounced than that of **1**. At least two other indenyl complexes [$(C_9H_7)_2Ni$][18d] ($\Delta_{M-C} = 0.418$ Å, HA = 13.9°, FA = 13.1°) and [$(C_9H_7)_2V(CO)_2$][25] ($\Delta_{M-C} = 0.498$ Å) show a similar distortion.

The hydrotris(3,5-dimethylpyrazolyl)borate ligand in **3** is also distorted with the pyrazole nitrogen *trans* to the phenyl ligands approximately 0.2 Å closer to the osmium than the pyrazole nitrogen *trans* to the nitride. This type of distortion in hydrotris(pyrazolyl)borate complexes is related to the trans influence of the other ligands present. Using values for the molybdenum−pyrazole bond distances in a series of related hydrotris(pyrazolyl)borate molybdenum complexes, Boncella and co-workers ranked a number of ligands with respect to their trans influence: alkylidyne ≈ oxo > imido ≈ alkylidene > amido > alkoxy > alkyl ≈ μ-oxo > triflate.[26]

Both the length of the osmium−nitride bond and the osmium−nitrogen stretching vibrations in the IR spectra give some indication of the ability of the cyclopentadienyl, indenyl, and hydrotris(3,5-dimethylpyrazolyl)borate ligands to donate electron density to the metal center. On the basis of the osmium−nitride bond distances, the order of ligand donor ability decreases in the order Cp > In ≈ Tp*. The stretching vibrations, ν_{Os-N}, observed in the IR spectra for these complexes support this trend. A similar trend is observed in comparison of the rhenium oxo complexes (Cp*)Re(O)($O_2C_2H_4$)[27] (Re−O = 1.696(2) Å; $\nu_{Re-O} = 907$ cm^{-1}) and (Tp)Re(O)(C_2O_2) (Re−O = 1.654(7) Å; $\nu_{Re-O} = 985$ cm^{-1}).[28] In contrast, the lengths of the vanadium−nitrogen bonds in the two analogous vanadium imido complexes TpV(N-*t*-Bu)Cl_2[29] (V−N = 1.638(2) Å) and CpV(N-*t*-Bu)Cl_2[30] (V−N = 1.590(4) Å) suggest that, in this case, the hydrotris(pyrazolyl)borate ligand is a better electron donor than the cyclopentadienyl ligand.

Conclusions

A series of Os(VI) diphenyl nitrido complexes containing the isoelectronic ligands cyclopentadienyl, indenyl, and hydrotris(3,5-dimethylpyrazolyl)borate have been synthesized and the molecular structure of each has

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[20] (a) Shrock, R. R.; LaPointe, A. M *Organometallics* **1993**, *12*, 3379−3381. (b) LaPointe, A. M.; Shrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1995**, *117*, 4802−4813.

[21] Huttner, G.; Brintzinger, H. H.; Bell, L. G. *J. Organomet. Chem.* **1978**, *145*, 329−333.

[22] Herrmann, W. A.; Felixberger, J. K.; Anwander, R.; Herdtweck, E.; Kiprof, P.; Riede, J. *Organometallics* **1990**, *9*, 1434−1443.

[23] Herrmann, W. A.; Weichselbaumer, G.; Paciello, R. A.; Fischer, R. A.; Herdtweck, E.; Okuda, J.; Marz, D. W. *Organometallics* **1990**, *9*, 489−496.

[24] Herrmann, W. A.; Herdtweck, E.; Flöel, M.; Kulpe, J.; Küsthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165−1182.

[25] Kowaleski, R. M.; Rheingold, A. L.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1986**, *108*, 2460−2461.

[26] Vaughan, W. M.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1995**, *14*, 1567−1577.

[27] Herrmann, W. A.; Marz, D.; Herdtweck, E.; Schäfer, A.; Wagner, W.; Kneuper, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 462−464.

[28] Brown, S. N.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4091−4100.

[29] Scheuer, S.; Fischer, J.; Kress, J. *Organometallics* **1995**, *14*, 2627−2629.

[30] Preuss, F.; Becker, H.; Häusler, H.-J. *Z. Naturforsch.* **1987**, *42B*, 881−888.

been determined. Both the Os−N stretching vibrations in the IR spectra and the Os−N distances in the X-ray structures of these three complexes suggest that the order of ligand donor ability for the isoelectronic ligands decreases in the order Cp > In ≈ Tp*. There is a significant distortion of both the cyclopentadienyl and indenyl ligands from η^5 toward η^3 coordination.

The relative ability of the cyclopentadienyl-type ligands to distort clearly affects the metal's π bonding to the nitrido ligand. We expect to see a similar trend in the imido complexes derived from alkylation of **1**−**3**. If π competition between the Cp-type ligand and the imido ligand is the primary factor influencing imido-group transfer reactions to unsaturated molecules, we should be able to observe it in the chemistry of this series. We are currently investigating the comparative reaction chemistry of osmium(VI) nitrido and imido complexes with these Cp-type ligands.

Experimental Section

All reactions were performed under a nitrogen atmosphere, using standard air-sensitive techniques with a Schlenk line or in a Vacuum Atmospheres glovebox unless otherwise stated. Diethyl ether, THF, hexane, and pentane were distilled from Na/benzophenone. Methylene chloride was distilled from CaH_2. Pyridine was distilled from KOH. All solvents were stored over 4 Å molecular sieves. Deuterated methylene chloride was purchased from Cambridge Isotope Laboratories and was used without further purification. All reagents were purchased from Aldrich. The complexes NaCp·DME,[31] [K][In],[32] $[K][HB(3,5\text{-}(CH_3)_2Pz)_3]$,[33] and $[N(n\text{-}Bu)_4][OsNPh4]$[15] were prepared according to literature procedures.

NMR spectra were recorded on a Varian Unity 500 spectrometer. Chemical shifts for the ^1H and ^{13}C NMR spectra were referenced to internal solvent resonances. IR spectra were recorded on a Perkin-Elmer 1600 Series FTIR. Elemental analyses were performed by the University of Illinois microanalytical service.

Preparation of $[PPh_4][Os(N)Cl_2Ph_2]$. A solution of $[PPh_4][OsNPh_4]$ (0.100 g, 0.117 mmol) in 30 mL of CH_2Cl_2 was prepared. Two equivalents of anhydrous HCl (0.235 mL of a 1.0 M HCl in ether, 0.235 mmol) was added, and the solution turned from a bright yellow to orange. After 10 min, the solvent was removed in vacuo, leaving the product as an orange oil. The product was recrystallized from THF/hexane; yield 0.086 g, 95.7%. Anal. Calcd for $OsNC_{36}H_{30}Cl_2$: C, 56.25; H, 3.93; N, 1.82. Found: C, 56.22; H 4.00; N, 1.67.

Preparation of $CpOs(N)Ph_2$. A solution of $[PPh_4][Os(N)Ph_2Cl_2]$ (0.100 g, 0.130 mmol) in 20 mL of CH_2Cl_2 was prepared. An excess of pyridine (20 drops) was added to the solution. Upon addition, the solution turned a darker orange color. After the mixture was stirred for 5 min, 2 equiv of $AgBF_4(NCMe)_4$ (0.093 g, 0.260 mmol) was added to the solution. Almost immediately the solution lightened to a reddish orange and a white precipitate formed. After 30 min, the solution was filtered through Celite and the solvent was removed from the filtrate in vacuo, leaving an orange oil. The $[Os(N)Ph_2(py)_2][BF_4]$ was used without further purification. The orange oil was then dissolved in 20 mL of THF, and NaCp·DME (0.024 g, 135 mmol) was added. The solution was stirred for 1 h and then filtered through Celite. The solvent was removed in vacuo. The residue was then dissolved in 1 mL of CH_2Cl_2, and 30 mL of hexane was added. The solution was concentrated to 15 mL and then filtered through Celite. Orange crystals were obtained by the slow evaporation of the hexane solution at −30 °C, or alternatively crystals could be obtained in a similar manner from pentane; yield 0.010 g, 18.2%. IR (KBr pellet, cm^{-1}): 3106 (w), 3045 (w), 1569 (m), 1560 (m), 1473 (m), 1458 (m), 1288 (w), 1080 (m, ν_{Os-N}), 1015 (m), 810 (w), 732 (s), 695 (m), 650 (w). ^1H NMR (500 MHz, CD_2Cl_2, 22.9 °C): δ 7.45 (m, 4H), 7.04 (m, 6H), 5.95 (s, 5H, $C_5\mathbf{H}_5$). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2, 23.0 °C): δ 147.06, 127.84, 125.39, 120.12, 97.30. Anal. Calcd for $OsNC_{17}H_{15}$: C, 48.21; H, 3.57; N, 3.31. Found: C, 47.78; H 3.56; N, 3.25.

Preparation of $InOs(N)Ph_2$. $[Os(N)Ph_2(py)_2][BF_4]$ (0.130 mmol) was prepared as described above. The orange oil was then dissolved in 20 mL of THF, and 1 equiv of KC_9H_7 (0.650 mL of a 0.2 M solution in THF, 0.130 mmol) was added. The solution stirred for 1 h and then was filtered through Celite. The solvent was removed in vacuo. The residue was then dissolved in 1 mL of CH_2Cl_2, and 30 mL of hexane was added. The solution was concentrated to 15 mL and then filtered through Celite. Orange crystals were obtained by the slow evaporation of the hexane solution at −30 °C, or crystals could be obtained in a similar manner from pentane; yield 0.020 g, 32%. IR (KBr pellet, cm^{-1}): 3110 (w), 3099 (w), 3064 (m), 3037 (m), 1569 (m), 1580 (m), 1473 (m), 1425 (w), 1369 (w), 1327 (w), 1231 (w), 1212 (w), 1191 (w), 1156 (w), 1092 (s, ν_{Os-N}), 1065 (w), 1018(m), 872 (m), 839 (m), 747 (m), 733 (s), 695 (s), 652 (w), 601 (w), 543 (w), 470 (w). ^1H NMR (500 MHz, CD_2Cl_2, 22.0 °C): δ 6.60 (m, H), 6.96−6.88 (m, H), 7.24−7.22 (m, H). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2, 22.0 °C): δ 144.86, 129.05, 128.48, 127.71, 127.58, 125.46, 123.94, 88.31, 77.50. Anal. Calcd for $OsNC_{21}H_{17}$: C, 53.26; H, 3.62; N, 2.96. Found: C, 53.51; H 3.77; N, 2.88.

Preparation of $Tp^*Os(N)Ph_2$. $[Os(N)Ph_2(py)_2][BF_4]$ (0.149 mmol) was prepared using $[N(n\text{-}Bu)_4][Os(N)Ph_2Cl_2]$ instead of $[PPh_4][Os(N)Ph_2Cl_2]$. The orange oil was then dissolved in 20 mL of THF, and 1 equiv of $K[HB(3,5\text{-}(CH_3)_2Pz)_3]$ (0.050 g, 0.149 mmol) was added. The solution was stirred for 5 h and then filtered through Celite. The solvent was removed in vacuo. The residue was then dissolved in 1 mL of CH_2Cl_2, and 30 mL of hexane was added. The solution was concentrated to 15 mL and then filtered through Celite. The hexane solution was stored at −30 °C for 24 h. The solvent was decanted from the dark red crystals, which were dried under vacuum for 30 min and then washed with diethyl ether; yield 0.023 g, 28%. IR (KBr pellet, cm^{-1}): 3058 (w), 3037 (w), 3002 (w), 2978 (w), 2964 (w), 2925 (w), 2550 (w), 1571 (m), 1560 (w), 1542 (s), 1508 (w), 1498 (w), 1490 (w), 1476 (w), 1448 (s), 1415 (s), 1381 (m), 1369 (s), 1208 (s), 1188 (m), 1094 (m, ν_{Os-N}), 1069 (s), 1043 (m), 1019 (m), 997 (w), 981 (w), 878 (w), 860 (m), 813 (m), 789 (m), 776 (m), 737 (s), 705 (m), 696 (m), 642 (m), 496 (w), 489 (w). ^1H NMR (500 MHz, CD_2Cl_2, 22.6 °C): δ 8.34 (m, 2H), 7.23 (m, 2H), 6.94 (m, 2H), 6.89 (m, 2H), 6.36 (m, 2H), 6.02 (s, 2H), 5.58 (s, 1H), 2.55 (s, 6H), 2.36 (s, 3H), 1.93 (s, 6H), 0.88 (s, 3H). $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2, 22.0 °C): δ 153.11, 152.88, 146.37, 144.81, 144.16, 143.13, 140.07, 127.24, 126.92, 124.96, 108.03, 107.57, 15.04, 15.00, 12.91, 12.60. Anal. Calcd for $OsN_7C_{27}H_{32}B$: C, 49.47; H, 4.92; N, 14.95. Found: C, 49.32; H 4.98; N, 14.69.

X-ray Diffraction Studies. Crystal and refinement details are given in the Supporting Information. Diffraction data were collected at 198 K on a Siemens Platform/CCD automated diffractometer using Mo Kα graphite-monochromated radiation (λ = 0.710 73 Å). All data crystals were mounted, using oil (Paratone-N, Exxon), to a thin glass fiber. The data were corrected for Lorentz and polarization effects and for absorption. Calculations were performed with the Siemens SHELXTL Plus version 5 software package. All structures were solved by direct methods.[34] Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The methyl

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(31) Braunstein, P.; Bender, R.; Jud, J. *Inorg. Synth.* **1989**, *26*, 341−343.

(32) Szajek, L. P.; Lawson, R. J.; Shapley, J. R. *Organometallics* **1991**, *10*, 357−361.

(33) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288−6294.

(34) Sheldrick, G. M. *SHELXS86: Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1986.

hydrogen atom positions in **3** were optimized by rotation about R−C bonds with idealized C−H, R−H, and H−H distances. Atomic parameters for the borate hydrogen in **3** were independently refined. All other hydrogen atoms were included as fixed idealized contributors.[35] For each structure, successful convergence of the full-matrix least-squares refinement on F^2 was indicated by the maximum shift/error for the last cycle. SHELXTL plots for each structure are shown in Figures 1, 2, and 3.

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Supporting Information Available: For **1**, **2**, and **3**, tables of crystal data collection and refinement parameters, atomic coordinates, thermal parameters, and all distances and angles (15 pages). Ordering information is given on any current masthead page.

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[35] Sheldrick, G. M. *SHELXL93: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.