this reflects increased mobility or alternate binding orientations of **4** in the mutated active site which allow for placement of the 5-*endo*-hydrogen near the oxidative intermediate. Addition of steric bulk (V295I mutant), however, resulted in a 54% decrease in *endo*-hydrogen abstraction from **4**, corresponding to a more restricted binding orientation. The steric bulk of a properly placed amino acid residue may afford greater differential stereoselectivity for the chemically equivalent, epimeric hydrogens at the 5-position of camphor, suggesting the utility of altering regio- and stereospecific oxidative catalysts by engineering the active site of cytochromes P-450s.

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Synthesis of a Highly Reactive (Benzyne)ruthenium Complex: C-C, C-H, N-H, and O-H Activation Reactions

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We report here the synthesis and chemistry of an exceptionally reactive ruthenium benzyne complex, $(PMe_3)_4Ru(\eta^2\text{-}C_6H_4)$ (**1**). The ruthenium–carbon bond in this molecule reacts with a wide range of organic substrates that are typically inert toward late transition-metal–carbon bonds, including those in benzyne complexes.[1] For example, complex **1** reacts cleanly with arylamine N–H bonds, water O–H bonds, and benzyl and aryl C–H bonds. It reacts with acetophenone to yield an O-bound enolate complex, inserts benzaldehyde cleanly, and cleaves the C–C bond of acetone.

The chemistry we have observed is summarized in Scheme I. The methyl phenyl compound *cis*-$Ru(PMe_3)_4(Ph)(Me)$ (**3**) can be prepared by treatment of *cis*-$Ru(PMe_3)_4(Me)(Cl)$ with PhMgBr. Compound **1** was produced in an NMR tube from the thermolysis of **3** at 110 °C in benzene in 94% yield by ^1H NMR spectroscopy (Cp_2Fe internal standard). Alternatively, the benzyne complex was isolated in gram quantities by the treatment of *trans*-$Ru(PMe_3)_4(Cl)_2$ with 2 equiv of PhMgBr in ether under argon to form the diphenyl compound *cis*-$Ru(PMe_3)_4(Ph)_2$ (**2**) in situ,[2] followed by thermolysis of the reaction solution for 8 h at 65 °C. Crystallization from pentane provided **1** in 46% yield.

Slow crystallization of a pentane solution of **1** gave crystals suitable for X-ray analysis; details of the determination are given in the Supplementary Material, and an ORTEP drawing is included in Scheme I. The length of the C–C bond coordinated to the ruthenium center is 1.355 (3) Å; the other C–C distances in the C_6H_4 ring are noted in Scheme I and range from 1.363 (4) to 1.411 (4) Å with an average value of 1.385 ± 0.015 Å. The two Ru–C distances of 2.072 (2) and 2.111 (2) Å are unequal as are the P(2)RuC(1) and P(4)RuC(2) angles of 101.79 (6)° and 117.06 (6)°; respectively. The Ru–C distances in **1** are ca. 0.07 Å shorter than the equivalent distances in $(PMe_3)_4Ru(\eta^2\text{-}C_2H_4)$[3] which is not unexpected since the hybridization at carbon is different in the two molecules.

The rate of thermolysis of methyl phenyl compound **3** at 110 °C in C_6D_6 solvent was measured in the presence of concentrations of PMe_3 between 1.70×10^{-3} M and 1.87×10^{-2} M. A linear inverse dependence of rate on phosphine concentration was observed. This is consistent with a mechanism requiring initial reversible dissociation of phosphine, leading to an intermediate having a coordinatively unsaturated ruthenium center which can then undergo oxidative addition of the ortho-C–H bond of the attached arene ring. Rapid elimination of methane and recoordination of phosphine would yield **1**. An alternative possibility involves reaction by a four-center mechanism,[4] but given the requirement for initial phosphine dissociation, the oxidative addition pathway appears to be the more reasonable hypothesis.

Despite its thermal stability at moderate temperatures, benzyne complex **1** is reactive toward a wide variety of mild reagents. For example, intermolecular C–H activation of arene solvent (the reverse of the benzyne formation reaction) was observed at 110 °C. Thermolysis of **1** in benzene-d_6 in a sealed, evacuated vessel for 14 h at 110 °C yielded $Ru(PMe_3)_4(\eta^2\text{-}C_6D_4)$, identified by ^1H NMR, ^2H NMR, and mass spectrometry. To distinguish between aryl ring exchange and H/D exchange mechanisms for this process, **1** was thermolyzed in toluene at 110 °C for 5 days. An initial product was observed after 10 h, and this was subsequently transformed thermally to the known orthometalated compound $Ru(PMe_3)_4(\eta^2\text{-}CH_2C_6H_4)$ (**4**).[5] This is consistent with **1** undergoing oxidative addition to benzylic as well as arene C–H bonds.

The high basicity of the metal center in complex **1** also makes it much more reactive than other benzyne complexes or transition-metal alkyls toward weakly acidic hydrogens. Reaction of complex **1** with *tert*-butyl alcohol yielded more than one product, but reaction with water for 1 h at room temperature in benzene yielded the phenyl hydroxide **5** in 67% yield.[6] Even H_2N-*p*-*tert*-Bu-C_6H_4 (pK_a = ca. 27)[7] reacts with **1** at 85 °C in toluene, leading to azametallacycle **7**. Presumably this process proceeds via initial cleavage of the arylamine N–H bond to give the unusual metal (aryl)(amido) complex **6**, followed by ortho-metalation.[8] Initial coordination of the amine to an open site at the metal center created by phosphine dissociation may explain the high reactivity of the amine.

Low-valent, electron-rich transition-metal complexes are typically unreactive toward insertion of the strong C–O double bond of ketones and aldehydes.[9,10] However, **1** reacts with benzaldehyde

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[1] (a) Gowling, E. W.; Kettle, S. F. A.; Sharples, G. M. *J. Chem. Soc., Chem. Commun.* **1968**, *21*. (b) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *110*, 1750. (c) Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992. (d) Arnold, J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1988**, 704.

[2] Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1979**, 472.

[3] Wong, W.-K.; Chiu, K. W.; Statler, J. A.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *Polyhedron* **1984**, *3*, 1255.

[4] For mechanistic studies of cyclometalations and β-hydride eliminations at the Cp_2Zr^{IV} center, see: Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3171 and references therein.

[5] (a) Statler, J. A.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1984**, 1731. (b) Calabrese, J. C.; Colton, M. C.; Herskovitz, T.; Klabunde, U.; Parshall, G. W.; Thorn, D. L.; Tulip, T. H. *Annals. New York Acad. Sci.* **1983**, *415*, 302.

[6] Only dinuclear tetrakis(trimethylphosphine)ruthenium hydroxide complexes have been synthesized: Jones, R. A.; Wilkinson, G.; Colquohoun, I. J.; McFarlane, W.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1980**, 2480. For monomeric ruthenium triphenylphosphine hydroxide complexes, see: Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546.

[7] Cox, R. A.; Stewart, R. *J. Am. Chem. Soc.* **1976**, *98*, 488.

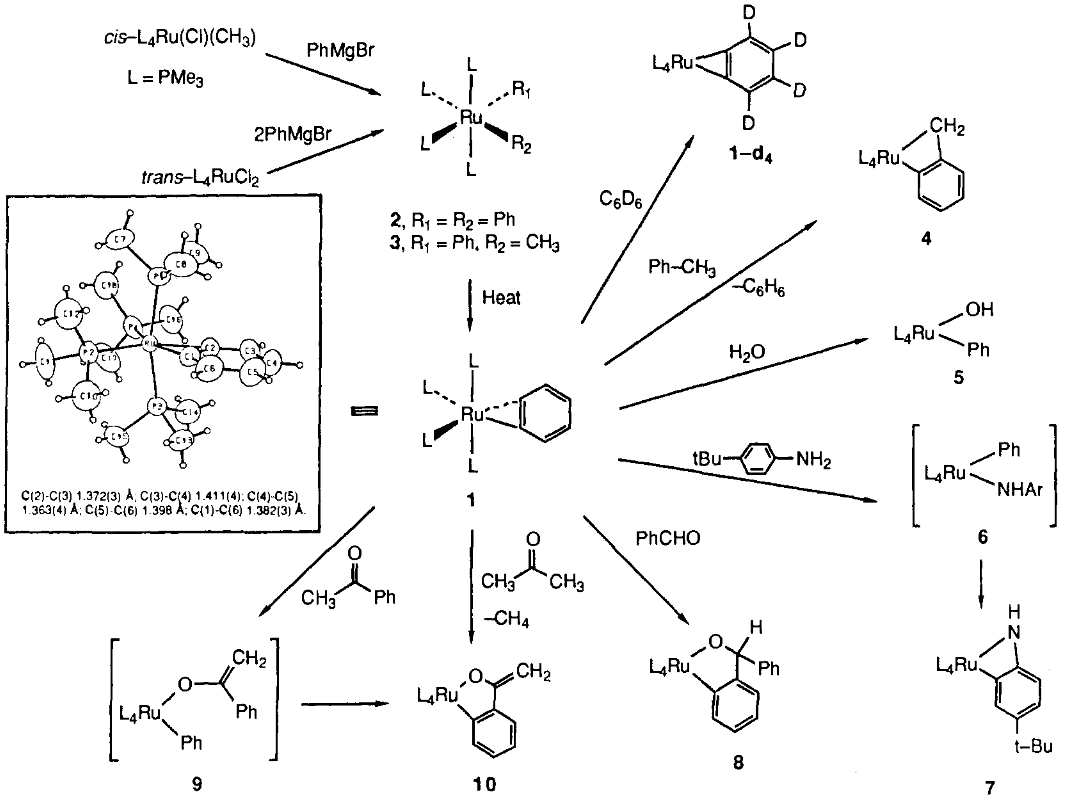
[8] Examples of late transition-metal compounds containing both alkyl or aryl and amide substituents include the following: (a) Bryndza, H. E.; Fultz, W. C.; Tam, W. *Organometallics* **1985**, *4*, 939. (b) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444. (c) Klein, D. P.; Hayes, J. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3704.

[9] Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986.

[10] Examples of fluorinated ketone insertions into late transition-metal hydride and alkyl bonds to yield late metal alkoxide complexes are found in the following: Hayashi, Y.; Komiya, S.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1984**, 1363.

0002-7863/89/1511-2717$01.50/0

Scheme I



at 45 °C for 1.5 days to give the single insertion product **8** in 33% isolated yield. Acetophenone reacts as a protic acid with **1** to provide the O-bound cyclometalated enolate complex **10** in 40% yield by ^{1}H NMR, presumably by way of the phenyl enolate complex **9**.[11] Remarkably, the reaction of **1** with acetone at 45 °C for 1.5 days led to the same product **10** (54% yield by ^{1}H NMR; 28% isolated), in this case extruding methane (identified by ^{1}H NMR spectrometry). This transformation results in the cleavage of an acetone C–C bond in addition to the formation of a new C–C bond in the organic ligand of the product.[12] Preliminary results of an X-ray structural study of **10** have confirmed its atom connectivity; full details of the structural and mechanistic studies will be published subsequently.

Reactions of other "late" transition-metal benzyne and cyclohexyne complexes (e.g., those in the Ni triad) are similar to those observed in analogous dialkyl compounds:[7] they undergo reactions only with acids at least as strong as alcohols and with unsaturated compounds containing weak double bonds, and typically they do not react with the C–H bonds of hydrocarbons. In contrast, early transition-metal (d^0) benzyne complexes which have been isolated are more reactive than their late metal counterparts.[13,14] Their chemistry is similar to that expected for early metal dialkyl compounds. Mechanistic information has indicated that their formation by intramolecular C–H activation proceeds by a four-center mechanism,[4] in contrast to the phosphine dissociation/oxidative addition pathway postulated here for our d^6 ruthenium complex. In summary, it appears that the electron-rich benzyne complex **1** is formed by a process typical of other low-valent, late transition-metal complexes, but its reactions are either unprecedented or similar to those seen with electrophilic, d^0 benzyne complexes. Further investigation of the scope and mechanisms of the transformations of complex **1** as well as exploration of the chemistry of its unusual reaction products is underway.

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(11) For oxygen-bound late transition-metal enolate complexes, see: (a) Slough, G. A.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1989**, *111*, 938. (b) Ito, Y.; Nakatsuka, N.; Kise, N.; Saegusa, T. *Tetrahedron Lett.* **1982**, *21*, 2873. (c) Kall'Antonia, P.; Graziani, M.; Lenarda, M. *J. Organomet. Chem.* **1980**, *186*, 131. Other oxygen-bound transition-metal enolate complexes consist of early metal compounds: (d) Moore, E. J.; Straus, D. A.; Armentrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068. (e) Planalp, R. P.; Andersen, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 7774. (f) Curtis, M. D.; Thanedar, S.; Butler, W. M. *Organometallics* **1984**, *3*, 1855. (g) Nakamura, E.; Shimada, J.-I.; Horiguchi, Y.; Kuwajima, I. *Tetrahedron Lett.* **1983**, *24*, 3341.

(12) Examples of C–C activation reactions include the following: (a) Suggs, J. W.; Cox, S. D. *J. Organomet. Chem.* **1981**, *221*, 199. (b) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1984**, *106*, 3054. (c) Suggs, J. W.; Wovkulich, M. J. *Organometallics* **1985**, *4*, 1101. (d) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1986**, *108*, 4679. (e) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (f) Crabtree, R. H.; Dion, R. P.; Gibbone, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222 and references therein. (g) Bunel, E.; Berger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976.

(13) (a) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (b) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7441. (c) Buchwald, S. L.; Watson, B. J.; Lum, R. T.; Nugent, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 7157. (d) Buchwald, S. L.; Sayers, A.; Watson, B. T.; Dewan, J. C. *Tetrahedron Lett.* **1987**, *28*, 3245. (e) McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263. (f) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1697. (g) Sarry, V. B.; Schaffernicht, R. *Z. Naturforsch.* **1981**, *86B*, 1238. (h) Sarry, V. B.; Singh, H.; Hahn, B.; Schaffernicht, R. *Z. Anorg. Allg. Chem.* **1979**, *456*, 181. (i) Bartlett, R. A.; Power, P. P.; Shoner, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 1966.

(14) Other d^0 benzyne complexes have been detected by labeling or trapping studies: (a) Masai, H.; Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 750. (b) Dvorak, J.; O'Brien, R. J.; Santo, W. *J. Chem. Soc., Chem. Commun.* **1970**, 411. (c) Kolomnikov, I. S.; Gobeeva, T. S.; Gorbachevskaya, V. V.; Aleksandrov, G. G.; Struckhov, Y. T.; Vol'pin, M. E. *J. Chem. Soc., Chem. Commun.* **1971**, 972. (d) Boekel, C. P.; Teuben, J. H.; De Liefde Meiger, H. J. *J. Organomet. Chem.* **1974**, *81*, 371; **1975**, *102*, 161. (e) Shur, V. B.; Berkovitch, E. G.; Vasiljeve, L. B.; Kudryavtsev, R. V.; Vol'pin, M. E. *J. Organomet. Chem.* **1974**, *78*, 127. (f) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189. (g) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659. (h) Erker, G.; Czisch, P.; Mynott, R.; Tsay, T.-H.; Kruger, C. *Organometallics* **1985**, *4*, 1310. (i) Chamberlain, L. R.; Kerschner, J. L.; Rothwell, A. P.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6471. (j) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232.

under Contract No. DE-AC03-76SF00098. The crystal structure analysis was performed by Dr. F. J. Hollander, staff crystallographer at the UC Berkeley X-ray crystallographic facility (CHEXRAY).

Supplementary Material Available: Spectroscopic and analytical data for complexes **1**, **1-d_4**, **3**, **4**, **5**, **7**, **9**, and **10** and details of the structure determination for complex **1**, including experimental description, ORTEP drawings showing full atomic numbering and packing in the crystal, and tables of crystal and data collection parameters, general temperature factor expressions (B's), positional parameters and their estimated standard deviations, root-mean-square amplitudes of anisotropic displacements, intramolecular distances and angles, and least-squares planes (18 pages); tables of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, and Reactivity of a Monomeric Pentamethylcyclopentadienyliridium(III)-Imido Complex

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We wish to report a simple, direct synthesis of Cp*IrNBu^t (Cp* = η^5-C$_5$Me$_5$). Despite its low formal oxidation state and coordination number, this Ir(III) compound is a monomer, as demonstrated by the first X-ray diffraction study on a group 9–11 terminal imido complex. It also exhibits unique reactivity at the MN linkage.[1,2]

Treatment of [Cp*IrCl$_2$]$_2$[3] with 4 equiv of LiNHBu^t in tetrahydrofuran affords the complex Cp*IrNBu^t, **1**, as yellow crystals in 80–90% yield. The reaction can be run on a 1 g scale; formation of the byproduct Bu^{t}NH$_2$ was confirmed by gas chromatography. In the ^{1}H NMR spectrum, the signal due to the *tert*-butyl methyl protons of **1** appears as a triplet (J = 1.6 Hz) as a result of coupling to ^{14}N. This coupling is characteristic of axially symmetric electron density at the nitrogen nucleus, as has been observed previously in imido complexes and in alkyl isonitriles, and suggests a linear M–N–C linkage.[4] Complex **1** also displays an IR stretching absorption characteristic of the imido ligand at 1258 cm^{-1} (the exact assignment must await ^{15}N labeling studies[5]) and was further characterized by ^{13}C NMR spectrometry and elemental analysis. The mass spectrum shows molecular ions at m/e 399 and 397 for the two iridium-containing isotopomers.

The monomeric nature of **1** suggested by the ^{1}H NMR and mass spectra was confirmed by an X-ray diffraction study performed on a single yellow, blocky crystal obtained by crystallization from pentane at −30 °C.[6] As shown in the ORTEP diagram included in Scheme I, complex **1** adopts a "one-legged piano stool" or "pogo-stick" geometry. The nearly linear Ir–N–C angle (177.2 (5)°) is consistent with Ir–N multiple bonding; the short Ir–N bond length (1.712 (7) Å) is similar to the value (1.68 Å) predicted by Nugent and Haymore for an Ir–N triple bond.[7] We therefore suggest that the strong π-donor imido ligand functions formally as a four-electron donor, making **1** an 18-electron complex.

Complex **1** undergoes a number of unprecedented reactions. In contrast to the behavior of the transient iridium–imido complex[8] [Ir(NH$_3$)$_5$NH]$^{3+}$, **1** is nucleophilic at nitrogen: it reacts with an excess of methyl iodide to form [Cp*IrI$_2$]$_2$[9] and [Me$_3$NBu^t]$^+$I$^-$.[10] The imido complex interacts with 2 equiv of *tert*-butyl isocyanide to form Cp*Ir(CNBu^t)(C(NBu^t)$_2$), **2**, in which one isocyanide has added across the Ir–N multiple bond to form a carbodiimide,[11] and the resulting 16-electron complex has been trapped by another isocyanide. Addition of 1 equiv of isocyanide affords a 1:1 mixture of **1** and **2**. Similarly, compound **1** undergoes a coupling-trapping reaction with 2 equiv of CO to form the carbonyl isocyanate complex **3** [ν_{CO} = 1956 and 1801 cm^{-1}; ^{13}C NMR δ 174.68 and 143.46 ppm].

Metal carbenes are known to undergo [2 + 2] cycloadditions with unsaturated substrates to form metallacycles.[12] Despite the isoelectronic nature of the imido and carbene ligands, this is a novel type of reaction for metal–imido complexes.[13] Reaction of **1** with carbon dioxide in pentane solution yields red crystals of **4**. This material exhibits spectral properties consistent with the structure illustrated in Scheme I [IR ν_{CO} = 1708 cm^{-1} (C$_6$H$_6$ solution); ^{13}C NMR δ 170.92 for the CO$_2$ carbon; MS parent ion at m/e 443/441]. Crystals of **4** suitable for X-ray analysis were obtained by vapor diffusion of hexamethyldisiloxane into toluene at −30 °C.[14] The structure demonstrates that formal [2 + 2]

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(1) For general references to organometallic imido chemistry, see: (a) Nugent, W. A. *Inorg. Chem.* **1983**, *22*, 965 and references therein. (b) Chan, D. M.-T.; Fultz, W. C.; Nugent, W. A.; Roe, D. C.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 251. (c) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123. (d) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Chapter 13.4. (e) Recently reactive imidozirconium complexes have been prepared: Walsh, P. J.; Hollander, F.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. Cummins, C. C.; Baxter, S. M.; Wolczanski, P. D. *J. Am. Chem. Soc.* **1988**, *110*, 8731.

(2) For examples of imido compounds of the late (groups 9–11) transition metals see: monomeric complexes with terminal imido ligands: (a) Ashley-Smith, J.; Green, M.; Mayne, N.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1969**, 409. (b) McGlinchey, M. J.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1970**, 1265. (c) Ashley-Smith, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1805. Dimeric μ_2-bridging complexes: (d) Meij, R.; Stufkens, D. J.; Vrieze, K.; Brouwers, A. M. F.; Overbeek, A. R. *J. Organomet. Chem.* **1978**, *155*, 123. (e) Sharp, P. R.; Ge, Y.-W. *J. Am. Chem. Soc.* **1987**, *109*, 3796. μ^3-Bridging trimeric clusters: (f) Otsuka, S.; Nakamura, A.; Yoshida, T. *Inorg. Chem.* **1968**, *7*, 261. (g) Muller, J.; Dorner, H.; Kohler, F. H. *Chem. Ber.* **1973**, *106*, 1122. (h) Abel, E. W.; Blackmore, T.; Whitley, R. S. *Inorg. Nucl. Chem. Lett* **1974**, *10*, 941. (i) Gall, R. S.; Connelly, N. G.; Dahl, L. F. *J. Am. Chem. Soc.* **1974**, *96*, 4017. (j) Bedard, R. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 5942. (k) Wakatsuki, Y.; Okada, T.; Yamazaki, H.; Cheng, C. *Inorg. Chem.* **1988**, *27*, 2958.

(3) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

(4) See ref 1c, p 143, and references therein, and Fjare, D. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 1572.

(5) Osborne, J. H.; Trogler, W. C. *Inorg. Chem.* **1985**, *24*, 3098.

(6) The X-ray diffraction study was carried out at the University of California, Berkeley, X-ray diffraction facility (CHEXRAY). Crystal data: *Pbcm*, V = 1528.2 (7) Å^3, Mo Kα λ = 0.71073 Å, μ_{calcd} = 86.8 cm^{-1}, d_{calcd} = 1.73 g cm^{-3}, a = 9.3284 (16) Å, b = 13.2916 (19) Å, c = 12.3250 (19) Å, T = 25 °C, Z = 4; the final residuals for 83 variables refined against the 873 data for which $F^2 > 3\sigma(F^2)$ were R = 2.06%, wR = 2.60%, and GOF = 1.168. The R value for all 1053 data was 3.32%. Details of the structure determination are provided as Supplementary Material.

(7) Reference 1c, p 134. This number was estimated using Pauling's relative metallic sizes and the typical Re$\equiv$NR bond length of 1.69 Å.

(8) Lane, B. C.; McDonald, J. W.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 3786.

(9) (a) Booth, B. L.; Haszeldine, R. N.; Hill, M. *J. Organomet. Chem.* **1969**, *16*, 491. (b) Gill, D. S.; Maitlis, P. M. *J. Organomet. Chem.* **1975**, *87*, 359.

(10) An authentic sample was prepared by repeated deprotonation and methylation of Bu^{t}NH$_2$. For the similar reaction of a Mo–imido complex, see: Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 2409.

(11) Precedent for imido-isocyanide coupling to form carbodiimide: Otsuka, S.; Aotoni, Y.; Tatsuno, Y.; Yoshida, T. *Inorg. Chem.* **1976**, *15*, 656.

(12) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, University Science Books: Mill Valley, CA, 1987; Chapter 16, and references therein.

(13) Formation of metallacycles has been observed with imidozirconocene complexes (see ref 1e), and with imidoboranes RB$\equiv$NR′: cf. Paetzold, P.; Delpy, K.; Hughes, R. P.; Herrmann, W. A. *Chem. Ber.* **1985**, *118*, 1724. For the reaction of a Fischer carbene and an azobenzene in which a Cr–imido complex may be formed via a metallacycle, see: Hegedus, L. S.; Kramer, A. *Organometallics* **1984**, *3*, 1263. A metallacycle has also been proposed as the initial product of the reaction between a Ta– or Nb-alkylidene complex and an imine: Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 3077.