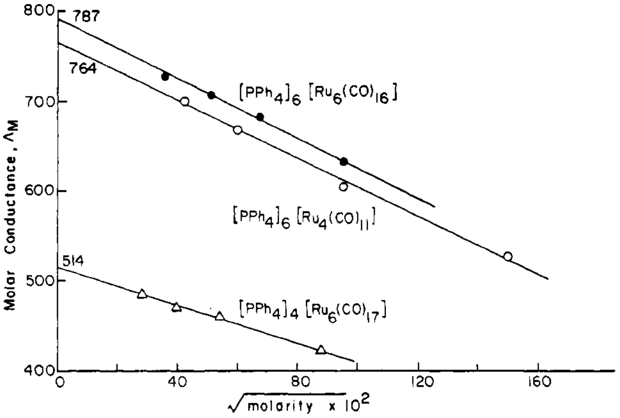


Figure 1. Molar conductivities in acetonitrile.

$(C_6H_5)_4]_4[Ru_6(CO)_{17}]$ are in accord with values for 6:1 and 4:1 electrolytes.[5]

In a typical preparation of the sodium salt of $[Ru_4(CO)_{11}]^{6-}$, a 0.532-mmol quantity (0.340 g) of $Ru_3(CO)_{12}$ was allowed to react with 2.402 mmol (0.495 g) of $Na[(C_6H_5)_2CO]$ in THF at 60 °C for 4 days. During this time 1.86 mmol of CO was produced (98% of theory based on reaction 1). The sodium salt that was isolated was heavily solvated with THF (ca. 6:1 THF/$Na_6[Ru_4(CCO)_{11}]$). It was extremely air sensitive, inflaming in air when in contact with tissue paper. From a metathesis reaction of $[P(C_6H_5)_4]Br$ in CH_3CN this salt was converted to $[P(C_6H_5)_4]_6[Ru_4(CO)_{11}]$ in 76% yield (based on initial amount of $Ru_3(CO)_{12}$). Anal. Calcd for $C_{155}H_{120}O_{11}P_6Ru_4$: C, 67.73; H, 4.60; P, 6.76; Ru, 14.71. Found: C, 66.36; H, 4.65; P, 6.47; Ru, 14.63.

Procedures for preparing the sodium and tetraphenylphosphonium salts of $[Ru_6(CO)_{17}]^{4-}$ and $[Ru_6(CO)_{16}]^{6-}$ were generally similar to those described above. The only significant difference involved choice of molar ratio of reactants consistant with the desired product (reactions 2 and 3). The salts $[P(C_6H_5)_4]_4[Ru_6(CO)_{17}]$ and $[P(C_6H_5)_4]_6[Ru_6(CO)_{16}]$ were isolated in 82% and 78% yields (based on initial amount of $Na_2[Ru_6(CO)_{18}]$. Anal. Calcd for $C_{113}H_{80}O_{17}P_4Ru_6$: C, 55.62; H, 3.30; P, 5.08; Ru, 24.85. Found: C, 55.49; H, 3.64; P, 4.98; Ru, 24.39. Anal. Calcd for $C_{160}H_{120}O_{16}P_6Ru_6$: C, 62.17; H, 3.91; P, 6.01; Ru, 19.62. Found: C, 61.86; H, 4.21% P, 6.03, Ru, 19.75.

Terminal and bridging carbonyl groups in all of the tetraphenylphosphonium salts are indicated by infrared spectra (in CH_3CN) in the carbonyl stretching region: $[P(C_6H_5)_4]_6[Ru_4(CO)_{11}]$, 1940 (s, sh), 1910 (s, br), 1710 (m, br) cm^{-1}; $[P(C_6H_5)_4]_4[Ru_6(CO)_{17}]$, 1970 (s), 1955 (m, sh), 1750 (w), 1660 (vw), 1590 (vw) cm^{-1}; $[P(C_6H_5)_4]_6[Ru_6(CO)_{16}]$, 1955 (w, sh), 1903 (s), 1830 (w, sh), 1720 (w, br) cm^{-1}.

Carbon-13 NMR spectra of a 50% ^{13}C-enriched sample of $Na_6[Ru_4(CO)_{11}]$ in THF-d_8 were recorded at 25 and -90 °C. A slow-exchange limit was not obtained. At room temperature a single sharp resonance was observed at 234 ppm. When this sample was cooled, three resonances at 228, 217, and 211 ppm were observed in the terminal CO region and peaks due to bridging carbonyls[6] in the region 279–295 ppm were beginning to rise from the base line. For $Na_4[Ru_6(CO)_{17}]$ ^{13}C NMR spectra were recorded at 25 and -50 °C. Low-temperature studies were limited due to precipitation of the salt. At room temperature a single resonance was observed at 228.7 ppm, indicating the complete equivalence of all carbonyl groups. When the sample was cooled to -50 °C, three resonances of 228.7, 218.6, and 212.0 ppm and a signal just emerging from the base line at 279 ppm were observed. Carbon-13 NMR spectra of $[PPh_4]_6[Ru_6(CO)_{16}]$ in CH_3CN exhibited one signal at 228.6 ppm at room temperature.

The sodium salts of the anions $[Ru_4(CO)_{11}]^{6-}$, $[Ru_6(CO)_{17}]^{4-}$, and $[Ru_6(CO)_{16}]^{6-}$ were protonated by using stoichiometric amounts of HCl in THF at -78 °C. Sodium chloride precipitated from the protonated solutions. At room temperature these solutions decomposed to give CO, H_2, and a mixture of nonvolatile products that are undergoing further study.

Acknowledgment. We thank the National Science Foundation for support of this work through Grant CHE 79-18149. The 300-MHz FT NMR spectra were obtained at The Ohio State University Chemical Instrument Center (funded in part by National Science Foundation Grant CHE-7910019). We also thank Madhav Chavan for helping with the conductivity experiments.

Registry No. $Ru_3(CO)_{12}$, 15243-33-1; $Na_2[Ru_6(CO)_{18}]$, 85781-89-1; $Na[(C_6H_5)_2CO]$, 3463-17-0.

---

(5) (a) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81. (b) Quagliano, J. V.; Summers, J. T.; Kida, S.; Vallarino, L. M. *Inorg. Chem.* **1964**, *3*, 1557.

(6) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1.

Organolanthanide and Organoyttrium Hydride Chemistry. 4. Reaction of Isocyanides with $[(C_5H_4R)_2YH(THF)]_2$ To Form a Structurally Characterized *N*-Alkylformimidoyl Complex[1]

William J. Evans,*[2a,b] James H. Meadows,[2b] William E. Hunter,[2c] and Jerry L. Atwood*[2c]

Departments of Chemistry, The University of Chicago
Chicago, Illinois 60637
University of California
Irvine, California 92717
and University of Alabama
University, Alabama 35486

Received June 1, 1983

Summary: The yttrium hydrides $[(C_5H_4R)_2YH(THF)]_2$ react with *tert*-butyl isocyanide to form $\{(C_5H_4R)_2Y[HC{=}NC(CH_3)_3]\}_2$, in which both C and N formimidoyl atoms coordinate to the yttrium.

The reaction of organometallic alkyls and hydrides with isocyanides has acquired significant interest in recent years due to the formal electronic analogy of isocyanides and carbon monoxide.[3-9] Reactivity ranging from simple ad-

---

(1) Presented in part at the "184th National Meeting of the American Chemical Society", Kansas City, MO, Sept 1982; American Chemical Society: Washington DC, 1982; INOR 213.

(2) (a) Camille and Henry Dreyfus Teacher-Scholar. Alfred P. Sloan Research Fellow. To whom correspondence should be addressed at the University of California. (b) University of Chicago. (c) University of Alabama.

(3) (a) Wolczanski, P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 6450–6452. (b) Wolczanski, P.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121–127.

(4) Yamamoto, Y.; Yamasaki, H. *J. Organomet. Chem.* **1970**, *24*, 717–724.

(5) (a) Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1977**, *99*, 6544–6550. (b) Adams, R. D.; Chodosh, D. F. *Inorg. Chem.* **1978**, *17*, 41–48. (c) Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 2579–2587. (d) Adams, R. D.; Golembeski, N. M. *Inorg. Chem.* **1978**, *17*, 1969–1976.

(6) Kuty, D. W.; Alexander, J. J. *Inorg. Chem.* **1978**, *17*, 1489–1494.

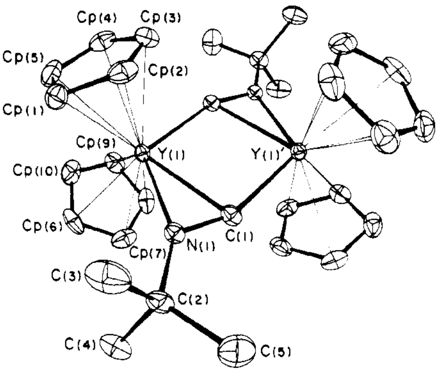


Figure 1. ORTEP plot of the molecular structure of $\{(C_5H_5)_2Y[HC{=}NC(CH_3)_3]\}_2$, **4a**. Y–Cp distances range from 2.659 (6) to 2.697 (6) Å with an average of 2.68 Å. N(1)–C(2) is 1.504 (6) Å. Selected angles (°) include Y(1)–C(1)–Y(1)′ = 89.9 (1), C(1)–Y(1)–C(1)′ = 90.1 (2), Y(1)–C(1)–N(1) = 65.4 (3), Y(1)–N(1)–C(1) = 84.6 (3), C(1)–N(1)–C(2) = 124.3 (4), and ring centroid –Y–ring centroid = 127.2.

duct formation or ligand substitution to formation of η^1-, η^2-, and η^3-N-substituted formimidoyl (HC(=NR)–) and alkyl and aryl imidoyl (RC(=NR)–) ligands has been observed. Although several alkyl and aryl imidoyl complexes have been characterized crystallographically,[10] the only formimidoyl complexes studied by X-ray diffraction have been $Ru(\eta^1\text{-}HC{=}NC_6H_4CH_3)(CO)[P(C_6H_5)_3]_2(CH_3CO_2)$, **1**,[13] $Os_3(\mu_3\text{-}\eta^2\text{-}HC{=}NC_6H_5)(CO)_9H$, **2a**, and $Os_3(\mu\text{-}\eta^2\text{-}HC{=}NC_6H_5)(CO)_9[P(OCH_3)_3]H$, **2b**.[5c] Structural studies involving formimidoyl complexes of the electropositive metals early in the transition series have not been reported. We present here the first structural data on a formimidoyl complex of an electropositive metal and describe a new coordination mode for this ligand.

As part of our investigation of the chemistry of lanthanide and yttrium hydrides,[14-16] we have examined the reaction of the neutral dimeric hydrides $[(C_5H_4R)_2YH(THF)]_2$ (R = H, **3a**; R = CH_3, **3b**)[14] with isocyanides. *tert*-Butyl isocyanide was most extensively investigated due to the steric bulk and single ^1H NMR resonance of the substituent. Typically, 2 equiv of the isocyanide (0.90 mmol in 3 mL of THF) are added slowly to a suspension of the dimer **3a** (0.43 mmol) in THF (20 mL) at room temperature under inert-atmosphere conditions (eq 1). **3a**

$$\underset{\textbf{3}}{[(C_5H_4R)_2YH(THF)]_2} + (CH_3)_3CNC \xrightarrow{THF} \{(C_5H_4R)_2Y[HCNC(CH_3)_3]\}_2 \quad (1)$$

4a, R = H
4b, R = CH_3

dissolved during the addition as the solution became yellow and then orange. After the solution is stirred 1 h, solvent is removed and the orange powder is washed with pentane. The reaction product **4a** can be extracted into toluene in 70–80% yield and was characterized by ^1H and ^{13}C NMR spectroscopy.[17] Recrystallization from toluene/pentane gives colorless prisms of **4a** characterized by complexometric analysis,[18] IR spectroscopy,[18] and X-ray diffraction.[19] A deuterium substituted analogue, **4a′**, was prepared analogously from $[(C_5H_5)_2YD(THF)]_2$ for spectroscopic purposes.[17,18] A solution of **3b** in THF reacts similarly to form the methylcyclopentadienyl analogue **4b**.[20]

Analytical and spectroscopic data suggested that **4** was the formimidoyl dimer $\{(C_5H_4R)_2Y[C(H){=}NC(CH_3)_3]\}_2$. IR absorptions at 1540, 1528, and 1532 cm^{-1} for **4a**, **4a′**, and **4b**, respectively, were indicative of C=N and absorptions at 2765 cm^{-1} for **4a** and 2020 cm^{-1} for **4a′** were consistent with a CH(CD) stretch in a formimidoyl ligand.[7,21] The Y–H and Y–C coupling in the NMR spectra suggested a dimeric structure in both toluene and THF solution.[17]

The X-ray diffraction study of **4a** confirmed the composition of the complex and revealed the details of the formimidoyl coordination geometry (Figure 1). The coordination sphere of each yttrium atom contains two cyclopentadienyl rings, a formimidoyl carbon–nitrogen unit bonded edge on, and a carbon atom from the other formimidoyl ligand in the dimer. The two yttrium atoms in

---

(7) (a) Christian, D. F.; Clark, G. R.; Roper, W. R.; Waters, J. M.; Whittle, K. R. *J. Chem. Soc., Chem. Commun.* **1972**, 458–459. (b) Christian, D. F.; Clark, H. C.; Stepaniak, R. F. *J. Organomet. Chem.* **1976**, *112*, 209–225.

(8) DeBoer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1979**, *166*, 193–198.

(9) Mays, M. J.; Prest, D. W.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 171–173.

(10) $(\eta^1\text{-}CH_3CNC_6H_4Cl)PtI[P(C_6H_5)_3]$,[11] $(\eta^2\text{-}CH_3CNC_6H_5)Mo(C_5H_5)(CO)_2$,[5b] $(\eta^1\text{-}CH_3CNC_6H_5)Mo(C_5H_5)(CO)_2[P(OCH_3)_3]$,[5b] $(\mu\text{-}\eta^2\text{-}C_6H_5CNCH_3)Os_3(CO)_{10}H$,[5d] and $(\mu_3\text{-}\eta^2\text{-}CH_3CNH)Fe_3(CO)_9H$.[12]

(11) Wagner, K. P.; Treichel, P. M.; Calabrese, J. C. *J. Organomet. Chem.* **1974**, *71*, 299–308.

(12) Andrews, M. A.; van Buskirk, G.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7245–7254.

(13) Clark, G. R.; Waters, J. M.; Whittle, K. R. *J. Chem. Soc., Dalton Trans.* **1975**, 2556–2560.

(14) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008–2015.

(15) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2015–2017.

(16) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401–1403.

(17) ^1H NMR (500 MHz, C_6D_6): δ 5.93 (s, C_5H_5); 0.98 (s, $HC{=}NC(CH_3)_3$, 9.29 (t, J = 1.5 Hz, $HC{=}NC(CH_3)_3$ (cf. ref 3a and 7a). The spectrum of **4a′** is identical except the δ 9.29 resonance is absent. The triplet structure of the formimidoyl hydrogen may be due to (a) fortuitously equal coupling to both yttrium atoms (100% abundant ^{89}Y has $I = {}^1/_2$), (b) chemical exchange (not detected by variable-temperature studies), or (c) inequivalent coupling to both yttrium atoms that appears equivalent due to additional Y–Y or H–H coupling. Explanation c is supported by the fact that the formimidoyl resonance has a filled-in triplet structure rather than an ideal binomial triplet structure and the fact that computer simulation, assuming inequivalent Y–H coupling but allowing for additional coupling, nicely reproduces this feature. $^{13}C\{^1H\}$ NMR (50.31 MHz, THF/C_6D_6 = 10): δ 108.6 (s, C_5H_5), 29.4 (s, $HC{=}NC(CH_3)_3$), 60.6 (s, $HC{=}NC(CH_3)_3$), 217.0 (doublet of doublets, $^1J_{Y\text{-}C}$ = 35 Hz, $^1J'_{Y\text{-}C}$ = 5 Hz, $HC{=}NC(CH_3)_3$). Application of reasonable Y–Y and H–H couplings in the simulation of the ^{13}C spectrum showed no observable effect on the ^{13}C spectrum due to the larger values of Y-^{13}C coupling.

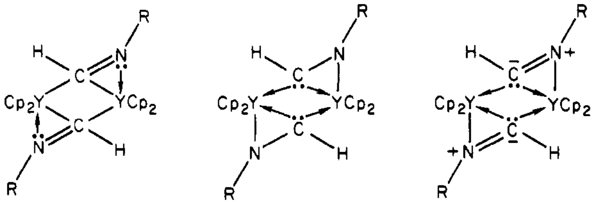
(18) Anal. Calcd for $YC_{15}H_{20}N$: Y, 29.35. Found: Y, 29.5. IR (KBr, cm^{-1}): 3075 (w), 2960 (w), 2870 (w), 2765 (w), 1760 (w), 1645 (w), 1540 (m), 1455 (m), 1385 (w), 1360 (s), 1290 (m), 1225 (w), 1188 (s), 1008 (s), 860 (w), 760 (s), 476 (m), 448 (m), 422 (w), 350 (m), 273 (w). The IR spectrum of **4a′** shows a shift of the absorption at 2765 cm^{-1} in **4a** to 2020 cm^{-1} (ν_{CH}/ν_{CD} = 1.37). The $\nu_{C=N}$ absorption also shifts from 1540 to 1528 cm^{-1}.

(19) Space group $P\bar{1}$. Cell constants: a = 8.496 (5) Å, b = 8.549 (5) Å, c = 10.459 (6) Å, α = 77.13 (4)°, β = 86.58 (4)°, and γ = 73.56 (4)° with Z = 1 dimer per unit cell and D_{calcd} = 1.42 g cm^{-3}. Least-squares refinement on the basis of 1729 observed reflections led to a final $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.035$. The diffraction experiment was conducted as described in: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45–53. An empirical absorption correction was done according to: Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957–1962. Anisotropic thermal parameters were those in SHELX, a system of computer programs for X-ray structure determination by G.M. Sheldrick, 1976. Although hydrogen atoms on the *tert*-butyl groups could be located, the hydrogen on C(1) was not found. Its presence is inferred from the IR and ^1H NMR data on **4a** and the deuterated analogue **4a′**.[17,18]

(20) Anal. Calcd for $YC_{17}H_{24}N$: Y, 26.87. Found: Y, 27.1, IR (KBr, cm^{-1}): 3070 (w), 2900 (m, br), 2720 (w), 1685 (w), 1580 (w), 1532 (m), 1455 (m), 1358 (s), 1286 (s), 1190 (s), 1025 (s), 930 (m), 870 (w), 820 (s), 750 (s), 618 (m), 569 (w), 466 (w), 440 (w), 414 (w), 320 (w). ^1H NMR (500 MHz, $C_6D_5CD_3$): δ 1.11 (s, $HC{=}NC(CH_3)_3$), 2.20 (s, $C_5H_4CH_3$), 5.95, 5.82, 5.60 (weakly coupled multiplets in 1:1:2 ratio, $C_5H_4CH_3$), 9.46 (t, J = 1.5 Hz, $HC{=}NC(CH_3)_3$). $^{13}C\{^1H\}$ NMR (THF/C_6D_6 = 10): δ 15.5 (s, $C_5H_4CH_3$), 29.7 (s, $HC{=}NC(CH_3)_3$), 61.1 (s, $HC{=}NC(CH_3)_3$), 107.0, 109.4, 109.6, 110.5 (all s, $\overline{C_4H_4C}CH_3$), 119.6 (s, $\overline{C_4H_4C}CH_3$), 218.1 (doublet of doublets, $^1J_{YC}$ = 35.5 Hz, $^1J'_{YC}$ = 4.7 Hz, $HC{=}NC(CH_3)_3$). The ^{13}C spectrum of **4b** in C_6H_6 is identical.

(21) Bellamy, L. J. "The Infrared Spectra of Complex Molecules"; Wiley: New York, 1964.

the dimer plus C(1), C(1)′, N(1), N(1)′, C(2), and C(2)′ are planar to within 0.007 Å. The C(1)–N(1) bond length of 1.275 (6) Å is reasonable for an sp^2-carbon nitrogen double bond.[22] It is intermediate between the 1.24 (1) Å length found in the monometallic η^1 complex 1[13] and the 1.415 (11) and 1.32 (10) Å distances found in the trimetallic η^2 complexes **2a** and **2b**,[5c] in which the formimidoyl carbon and nitrogen atoms are bound to two or three different osmium atoms.[23] The Y–C(1) and Y–C(1)′ distances of 2.545 (5) and 2.561 (5) Å compare well with the Y–(C) distances of 2.553 (10) and 2.537 (9) Å found in $[(C_5H_5)_2Y(\mu\text{-}CH_3)]_2$, **5**, which contains electron-deficient three-center two-electron methyl bridges.[24] The Y–Y distance of 3.607 (1) Å also is similar to that in **5**, 3.599 (8) Å, and to metal–metal distances in other electron-deficient bridged organoyttrium and organolanthanide dimers.[14,25] Hence, the carbon–nitrogen and carbon–yttrium distances are compatible with structure A in which the Y–N interaction is due to donation of a nitrogen lone pair to yttrium. Structure A is formally analogous to a stabilized formyl.[26]



$Cp = C_5H_5$; $R = C(CH_3)_3$

However, the Y–N distance of 2.325 (4) Å is much shorter than that expected for a =N:→Y bond[27] and is reasonable for an yttrium–nitrogen single bond.[29] An yttrium–nitrogen single bond requires the formimidoyl carbon to be carbene-like as shown in structures B and C. Structure B reiterates the similarity of isocyanides and CO and emphasizes the relationship of **4a** to η^2-formyl[30] and -acyl[31] complexes. Structural data on carbenes involved in three-center two-electron electron-deficient bonding have not been reported to our knowledge.

Given the coplanarity of C(1), N(1), and C(2), structure B is likely to contribute least to the bonding in **4**. Regardless of the relative contributions of A–C to the bonding, the structure of **4a** represents a new mode of formimidoyl coordination and the first crystallographically characterized example of η^2 coordination of a multiply bonded organic moiety within bonding distance of a transition group 3 metal center. Further studies of the reactivity of organoyttrium hydrides with unsaturated organic substrates are continuing.

Acknowledgment. For support of this research, we thank the Division of Basic Energy Sciences of the Department of Energy (W.J.E., J.H.M.) and the National Science Foundation (J.L.A., W.E.H.). We also thank the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Grant (to W.J.E.), and the Alfred P. Sloan Foundation for a Research Fellowship (to W.J.E.).

Registry No. **3a**, 80642-73-5; **3b**, 80658-44-2; **4a**, 86528-30-5; **4a′**, 86528-32-7; **4b**, 86528-31-6; $[(C_5H_5)_2YD(THF)]_2$, 80642-74-6; $(CH_3)_3CNC$, 7188-38-7.

Supplementary Material Available: Tables of bond distances, angles, final fractional coordinates, thermal parameters and observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

---

(22) *Spec. Publ.—Chem. Soc.* **1965**, *No. 18*. Sandorfy, C. In "The Chemistry of the Carbon Nitrogen Double Bond"; Patai, S., Ed.; Wiley: New York, 1970; Chapter 1.

(23) The C–N distance in **4a** is comparable to the 1.266 (12) and 1.287 (13) Å C–N distances found in the η^1-alkanimidoyl complexes $(CH_3CNC_6H_5)Mo(C_5H_5)(CO)_2[P(OCH_3)_3]$[5b] and $(CH_3CNC_6H_4Cl)PtI[P(C_6H_5)_3]_2$[11] and larger than the 1.233 (6) Å C–N length in $(\eta^2\text{-}CH_3CNC_6H_5)Mo(C_5H_5)(CO)_2$.[5b]

(24) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54–61.

(25) Atwood, J. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115–4119. Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 709–714.

(26) Belmonte, P.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 2858–2860 and references therein.

(27) Complex, metal–N distance (Å), metal radius minus Y^{3+} radius (Å),[28] reference: $(C_5H_5)_3YbNC_4H_4NYb(C_5H_5)_3$, 2.61 (1), −0.022, Baker, E. C.; Raymond, K. N. *Inorg. Chem.* **1977**, *16*, 2710–2714. $[C_5(CH_3)_5]_2Yb(NC_5H_5)_2$, 2.586 (7) and 2.544 (6), 0.05, Tilley, T. D.; Andersen, R. A.; Spencer, B.; Zalkin, A. *Ibid.* **1982**, *21*, 2647–2649. $La(bpy)_2(NO_3)$, 2.665 (10) and 2.658 (9), 0.181, Al-Karaghouli, A. R.; Wood, J. S. *Ibid.* **1972**, *11*, 2293–2299. $Eu(terpy)_3(ClO_4)_3$, 2.57 (1)–2.62 (1), 0.07, Frost, G. H.; Hart, F. A.; Heath, C.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1969**, 1421–1422. $Eu(phen)(acac)_3$, 2.645 (12) and 2.641 (8), 0.07, Watson, W. H.; Williams, R. J.; Stemple, N. R. *J. Inorg. Nucl. Chem.* **1972**, *34*, 501–508. $Ho(thd)_3(4\text{-picoline})_2$, 2.53 (3), 0.014, Horrocks, W. DeW., Jr.; Sipe, J. P., III; Luber, J. R. *J. Am. Chem. Soc.* **1971**, *93*, 5258–5260. $\{Sm[2.2.2\text{-crypt}]NO_3\}[Sm(NO_3)_5(H_2O)]$, 2.2748 (5), 2.779 (6) Å, 0.084, Burns, J. H. *Inorg. Chem.* **1979**, *18*, 3044. Comparisons using the radii of Shannon (Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751–767) similarly indicate the Y–N bond in **4a** is short compared to known =N:→Ln distances.

(28) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; 4th Ed.; Wiley: New York, 1980; pp 982, 1002.

(29) Y–N distances of 2.314 (9) and 2.382 (9) Å have been found in $\{(C_5H_5)_2Y[N{=}C(H)C(CH_3)_3]\}_2$, which has three-center Y–N–Y bridges: Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L., submitted for publication in *J. Am. Chem. Soc.*

(30) Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959–6962 and references therein.

(31) Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 706–708 and references therein.

Transition-Metal-anti-Bredt Olefin Complexes. Preparation and Reactions of Platinum(2+) and Palladium(2+) Complexes of Bicyclo[3.3.1]non-1-ene

Stephen A. Godleski,* Richard S. Valpey, and
Kurt B. Gundlach

Department of Chemistry, University of Rochester
Rochester, New York 14627

Received June 9, 1983

Summary: A solution-stable Pt(2+) complex of bicyclo[3.3.1]non-1-ene (**3**) has been prepared and spectroscopically characterized. NMR data reveal a substantial contribution from a metallocyclopropane structure. Reaction of **3** with a variety of Pd(2+) and Pt(2+) compounds reveals that the intermediate olefin complexes formed possess a tremendous facility for undergoing insertion reactions of M–Cl, M–H, and $M\text{–}CH_3$ bonds into the olefin.

A transition-metal-complexed anti-Bredt olefin[1] provides two extremely interesting avenues for investigation. The

---

(1) For a review on anti-Bredt olefins see: Fawcett, F. S. *Chem. Rev.* **1950**, *47*, 219. Keese, R. *Angew. Chem.* **1975**, *87*, 568; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 528. Buchanan, G. L. *Chem. Soc. Rev.* **1974**, *3*, 41. Shea, K. J. *Tetrahedron* **1980**, *36*, 1683.