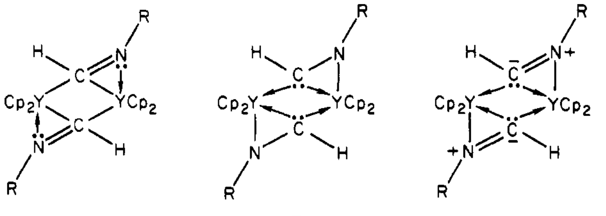
the dimer plus C(1), C(1)′, N(1), N(1)′, C(2), and C(2)′ are planar to within 0.007 Å. The C(1)–N(1) bond length of 1.275 (6) Å is reasonable for an $sp^2$-carbon nitrogen double bond.[22] It is intermediate between the 1.24 (1) Å length found in the monometallic $\eta^1$ complex 1[13] and the 1.415 (11) and 1.32 (10) Å distances found in the trimetallic $\eta^2$ 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]



A B C

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

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 $\eta^2$-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 $\eta^2$ 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.

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(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 $\eta^1$-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.

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# 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

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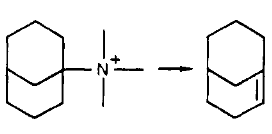
[1] For a review on anti-Bredt olefins see: Fawcett, F. S. *Chem. Rev.* **1950**, *47*, 219. Keese, R. *Angew. Chem.* **1975**, *87*, 568; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 528. Buchanan, G. L. *Chem. Soc. Rev.* **1974**, *3*, 41. Shea, K. J. *Tetrahedron* **1980**, *36*, 1683.

Table I. NMR Data for 3, 5, 6, and 2-Methyl-2-butene[a]

| | |
|---|---|
| 3 | $^{13}$C NMR $\delta$(C(1)) 148.25, $\delta$(C(2)) 125.77 ($J_{C(2)-H}$ = 160.6 Hz) $^1$H NMR 5.72 ppm ($H_a$, t, $J$ = 6.59 Hz) |
| 5 | $^{13}$C NMR $\delta$(C(1)) 120.45 ($J_{Pt-C(1)}$ = 211.6 Hz), $\delta$(C(2)) 84.25 ($J_{Pt-C(2)}$ = 202.9 Hz, $J_{C(2)-H}$ = 159.8 Hz) $^1$H NMR 5.54 ($H_a$, t, $J$ = 7.0 Hz, $J_{Pt-H}$ = 73.3 Hz) |
| 2-methyl-2-butene | $^{13}$C NMR $\delta$(C(1)) 132.0, $\delta$(C(2)) 118.4 ($J_{C(2)-H}$ = 151.3 Hz) |
| 6 | $^{13}$C NMR $\delta$(C(1)) 116.01 ($J_{Pt-C(1)}$ = 143.6 Hz, $\delta$(C(2)) 84.71 ($J_{Pt-C(2)}$ = 147.2 Hz, $J_{C(2)-H}$ = 154.4 Hz) $^1$H NMR 5.63 ppm ($H_a$, $J_{Pt-H}$ = 66.0 Hz) |

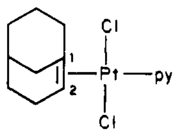
[a] All spectra determined in $CDCl_3$ at rt on Bruker WH-400.

first centers on the ability of a transition metal to interact with a bicyclic bridgehead olefin and provide effective stabilization by a reduction of the level of unsaturation at the olefin ligand.[2] Although stabilization of a variety of strained unsaturated species is precedented,[3-5] the nonplanarity of the $\pi$ system of an anti-Bredt olefin is quite unique and presents a distinctly different challenge to the metal. To date, the only examples of such species that have been reported are bis(phosphine)platinum(0) complexes of bicyclo[4.2.1]non-1-ene (1) and bicyclo[4.2.1]non-1(8)-ene (2).[7,8] The second aspect involves the nature of the chemistry that such species would undergo. For example, the usual mode of addition of nucleophiles to complexed olefins is by direct attack on the olefin ligand,[2] a mode that is largely prohibited by the bicyclic ring system of the anti-Bredt olefin. How such a species would compensate for the loss of this reaction pathway was most intriguing. Metal(II)–anti-Bredt complexes appeared to us to be particularly attractive targets to evaluate in this regard as the only reaction that is reported for 1 and 2 is olefin isomerization.[7] Inspired by these questions, we undertook the preparation of such a compound and would now like to report the first examples of metal(II) transition-metal–anti-Bredt olefin complexes and provide a preliminary account of their reactivity.

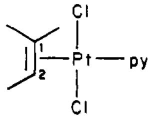


4 3

We chose as our prototypal anti-Bredt species bicyclo[3.3.1]non-1-ene (3) which was prepared by the pyrolysis of the ammonium salt 4 according to the method of Wiseman.[9] In the absence of any metal trapping agent, the only reaction 3 undergoes is a [2 + 2] dimerization ($t^{1/2}$ in $CDCl_3$ at room temperature is ~3 days). Olefin exchange with (ethylene)$PtCl_2$(pyridine) (1 equiv, 0.1 M in $CDCl_3$, 0 °C, driven by the removal of ethylene by bubbling Ar through the solution) provided complex 5 in quantitative yield. Complete $^{13}$C and $^1$H NMR characterization of 5 is given in Table I. Also included are data for the uncomplexed olefin 3 and for the (2-methyl-2-butene)-$PtCl_2$(pyridine) complex (6) as a model trisubstituted olefin. Immediately apparent on inspection of the NMR data is the exceptionally large $^{13}$C shift on complexation ($\Delta$(C)) of 3 and the abnormally high $^{195}$Pt–C and $^{195}$Pt–H couplings relative to the 2-methyl-2-butene model system 6: 5, $\Delta$(C(1)) 27.8 ppm, $\Delta$(C(2)) 41.5 ppm; 6, $\Delta$(C(1)) 14.7 ppm, $\Delta$(C(2)) 34.0 ppm; 5, $J_{Pt-C(1)}$ = 211.6 Hz, $J_{Pt-C(2)}$ = 202.9 Hz; 6, $J_{Pt-C(1)}$ = 143.6 Hz, $J_{Pt-C(2)}$ = 147.2 Hz. These data suggest a substantial contribution of a metallocyclopropane structure for 5.[10]



5



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Significantly, complex 5 is stable indefinitely[11] at room temperature, suggesting that the anticipated stabilization of this strained olefinic species was being fully realized.

A preliminary investigation of the chemistry of anti-Bredt olefin–transition-metal complexes has proven equally rewarding. Reaction of olefin 3 and $Pd(OAc)_2$ (1 equiv, 0.1 M in $CDCl_3$, 5 min, room temperature) or $Pd(CH_3CN)_2(Cl)_2$ (1 equiv, 0.1 M in THF-$d_8$, 5 min, room temperature) provided only the rearranged olefin 7 in quantitative yield,[12] reminiscent of the reaction of the Pt(0) complexes of 1 and 2. A likely mechanism for this isomerization was suggested by the further observation that reaction of 3 with $Pd(PhCN)_2(Cl)_2$ (5 equiv, 0.1 M in $CDCl_3$, room temperature, 20 min) gave not only 7 but also

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(2) A reduction of the level of unsaturation of olefins on complexation is generally understood via the Dewar–Chatt–Duncanson model of olefin–metal bonding and has been largely verified by spectroscopic investigation, see: Collman, J. P., Hegedus, L. S. "Principles and Applications of OrganoTransition Metal Chemistry"; University Science Books: Mill Valley, California, 1976.

(3) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750.

(4) Visser, J. P.; Ramakers, J. E. *J. Chem. Soc., Chem. Commun.* **1972**, 178.

(5) For other examples of transition metal stabilization of strained olefins, see: Jason, M. E.; McGinnety, J. A.; Wiberg, K. *J. Am. Chem. Soc.* **1974**, *96*, 6531. Evers, J.; Mackor, A. *Tetrahedron Lett.* **1978**, 2317.

(6) Stamm, E.; Becker, K. B.; Engel, P.; Ermer, O.; Keese, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 685.

(7) Stamm, E.; Becker, K. B.; Engel, P.; Keese, R. *Helv. Chim. Acta* **1979**, *62*, 2181.

(8) There is an additional example of an Fe(0) complexed *trans*-cyclononene bicyclic system, but we feel that this is not sufficiently strained to be a member of this class of complexes see: v. Buren, M.; Hansen, H. J. *Helv. Chim. Acta* **1977**, *60*, 2717.

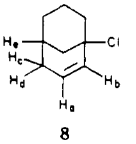
(9) Wiseman, J. R.; Pletcher, W. A. *J. Am. Chem. Soc.* **1970**, *92*, 956.

(10) $^{195}$Pt–H and $^{195}$Pt–C coupling constants are not included in the $^1$H and $^{13}$C NMR data for 1 and 2 and are not available for comparison to 5.

(11) A sample of 5 has been stored at room temperature and shows no sign of decomposition over 6 months. 5 exists as an amphorous light yellow solid; decomposition pt 144–145 °C. We are attempting to obtain crystals for X-ray analysis. Anal. Calcd for $C_{14}H_{19}NCl_2Pt$: C, 35.98; H, 4.10. Found: C, 35.88; H, 4.10.

(12) A sample of rearranged olefin 7 was prepared by an independent route and proved to be identical in all respects. See ref 26.

(13) 8 and 9 were collected by preparative GLC (mixture not separated) and characterized by $^1$H NMR (400 MHz, $CDCl_3$) and GC–MS. Typical runs were conducted with 10 mg (0.08 mmol) of 5. $^1$H NMR (8): 5.80 ($H_a$, d, t, $J$ = 10, 3 Hz), 5.71 ($H_b$, d, $J$ = 10 Hz), 2.30 ($H_c$, d, t, $J$ = 19, 3 Hz), 1.78 ($H_d$, d, d, $J$ = 19, 3 Hz), 2.24 ppm ($H_e$, t, $J$ = 3 Hz). $^1$H NMR (9): 5.73 ($H_a$, d, t, $J$ = 10, 3 Hz), 5.59 ($H_b$, d, d, $J$ = 10, 5 Hz), 2.75 ($H_c$, d, d, $J$ = 18, 2 Hz), 2.60 ($H_d$, d, d, $J$ = 5, 3 Hz), 2.52 ppm ($H_e$, d, d, $J$ = 18, 3 Hz). MS: *m/e* 158, 156, 115, 113. High-resolution MS: 156.6599 (calcd), 156.6586 (found).



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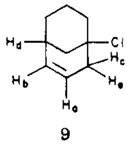

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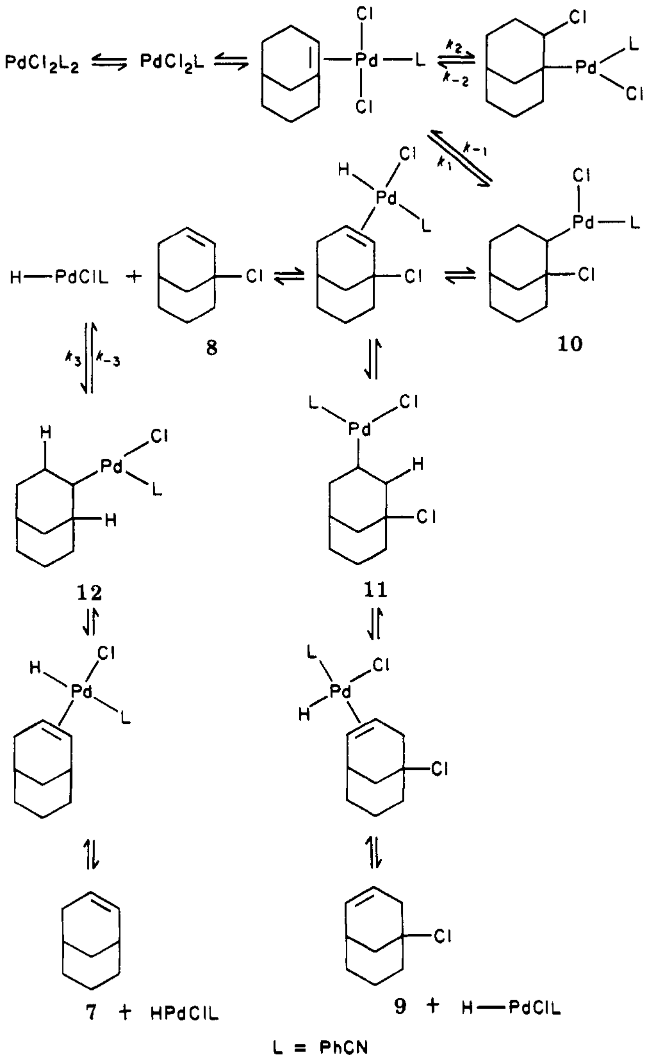
Scheme I. Proposed Mechanism for Formation of 7, 8, and 9



two bridgehead chlorinated olefins 8 and 9[13] (7, 8, and 9; 1:1:1 ratio, >95% total yield based on NMR analysis with internal standard). These products can be accounted for by the mechanism in Scheme I. Insertion of Pd–Cl into the olefin 3 produces the $\sigma$-Pd intermediate 10. The regiochemical preference for insertion is due presumably to steric effects ($k_1 > k_2$ or $k_1/k_{-1} > k_2/k_{-2}$). $\beta$-Hydride elimination from 10 provides 8. Production of a Pd–H species allows both for the observation of 9 via hydropalladation to give 11 followed by its dehydropalladation and for the observation of 7 by Pd–H insertion into the olefin 3 to give 12 followed by $\beta$-H elimination. The relative amounts of bridgehead-substituted olefins and rearranged olefins observed are determined by the rates of Pd–Cl ($k_1$) vs. Pd–H ($k_3$) insertion. For $Pd(OAc)_2$[14] and $Pd(CH_3CN)_2(Cl)_2$ $k_3 \gg k_1$ and only 7 is seen, and for $Pd(PhCN)_2(Cl)_2$ $k_3 \approx k_1$ and 7, 8, and 9 are all produced. Initial attempts to trap the $\sigma$-bound intermediate 10 by running the reaction under a CO atmosphere were unsuccessful.

The observation of 8 and 9 has additional mechanistic significance as unambiguous cis chloropalladation of olefins, as *must* be occurring in 3, is generally very difficult to prove[15] due to the possibility of competing trans (ligand) addition via nucleophilic attack of $Cl^-$. In addition, although the chloropalladation of allenes,[16] dienes,[17] alkynes,[18] and certain olefins[15] is known, the facility of the Cl–Pd insertion observed for 3 is quite unusual and may be due to the substantial $\sigma$ character in the Pd–C bonds of its complex.

This facility for insertion reactions was further demonstrated by the reaction of 3 with $Pd(Me)_2(PPh_3)_2$ (1 equiv in 0.1 M $CDCl_3$, room temperature 12 h) which yielded 7, 14, and 15[19] (5:2:1, >95% total yield based on GC analysis with internal standard) presumably via a mechanism comparable to that shown in Scheme I now initiated by Pd–Me insertion. When this reaction was repeated with $Pd(CD_3)_2(PPh_3)_2$ intact, incorporation of the $CD_3$ group into 14 and 15 was observed, eliminating the possibility of a $Pd{=}CH_2$ intermediate. Although alkylmetal olefin insertions are believed to be operating in Ziegler–Natta polymerizations,[20] direct observation of such reactions is relatively rare[21,22] especially for late transition-metal complexes.[23-25]

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[14] In the $Pd(OAc)_2$ reaction Pd–OAc insertion would be the presumed initiating step, $k_1$.

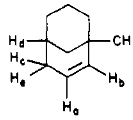
[15] Evidence suggesting cis chloropalladation of olefins has been provided in: Henry, P. M. *J. Org. Chem.* **1976**, *37*, 2443. See also: Green, M.; Hughes, R. P. *J. Chem. Soc., Chem. Commun.* **1974**, 686. Trans chloropalladation has been observed in: Wipke, W. T.; Goeke, G. L. *J. Am. Chem. Soc.* **1974**, *96*, 4244. Wiger, G.; Albelo, G.; Rettig, M. F. *J. Chem. Soc., Dalton Trans.* **1974**, 2242.

[16] See for example: Lupin, M. S.; Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 1687.

[17] See for example: Lukas, J.; Van Leeuwen, P. W. N. M.; Volger, H. C.; Kouwenhoven, A. P. *J. Organomet. Chem.* **1973**, *47*, 153.

[18] See for example: Mann, B. E.; Bailey, P. M.; Maitlis, P. M. *J. Am. Chem. Soc.* **1975**, *97*, 1275.

[19] **14** and **15** were collected by preparative GLC (mixture not separable) and characterized by $^1H$ NMR (400 MHz, $CDCl_3$) and GC–MS. Typical runs were conducted with 10 mg (0.08 mmol) of **5**. $^1H$ NMR (**14**): 5.76 ($H_a$, d, t, $J$ = 10, 3 Hz), 5.29 ($H_b$, d, d, d, $J$ = 10, 2, 1 Hz), 2.24 ($H_c$, d, d, d, d, $J$ = 16, 7, 3, 2 Hz), 2.05 ($H_d$, bt, $J$ = 7 Hz), 1.73 ($H_e$, d, d, t, $J$ = 16, 3, 1 Hz), 0.91 ppm ($CH_3$, s). $^1H$ NMR (**15**): 5.75 ($H_a$, d, t, $J$ = 9, 3 Hz), 5.60 ($H_b$, d, bt, $J$ = 9, 2 Hz), 2.28 ($H_c$, bt, $J$ = 8 Hz), 1.90 ($H_d$, d, d, d, $J$ = 15, 3, 1, Hz), 1.78 ($H_d$, d, d, d, $J$ = 15, 3, 2 Hz), 0.83 ($CH_3$, s). MS: *m/e* 136, 121, 93, 79. High-resolution MS: 136.2363 (calcd), 136.2349 (found).



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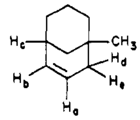

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[20] Proposal of Ziegler–Natta polymerization proceeding by alkylmetal–olefin insertion: Henrici-Olive, G.; Olive, S. *Top. Curr. Chem.* **1976**, *67*, 107. Thorn, D. L.; Hoffman, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079. Heck, R. F.; *Ibid.* **1968**, *90*, 5518. Cooke, M. P., Jr.; Parlman, R. M. *Ibid.* **1977**, *99*, 5222; **1975**, *97*, 6863. Booth, B. L.; Gardner, M.; Haszeldine, R. N. *J. Chem. Soc., Dalton Trans.* **1975**, 1856. James, D. E.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 1810. For alternative mechanisms see: McKinney, R. J. *J. Chem. Soc., Chem. Commun.* **1980**, 491. Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *Ibid.* **1978**, 604.

[21] Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 7003; **1979**, *101*, 3973.

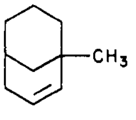
[22] Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337; **1982**, *104*, 6471.

[23] A variety of reactions are believed to involve Pd–C insertion into olefins, but alternative mechanisms proceeding by direct nucleophilic attack on the ligand are also possible. See: Maitlis, P. "The Organic Chemistry of Palladium"; Academic Press: New York, 1981; Vol. I, Chapter 1. Such attack is not possible in reactions of 3. The well-known Heck arylation reaction is believed to proceed via an insertion reaction of a ($\sigma$-aryl)palladium complex into an olefin but functions only for aryl, heterocyclic, vinyl, and benzyl species bound to the metal; see: Heck, R. F. *Pure Appl. Chem.* **1978**, *50*, 691.

[24] The presumed olefin–metal alkyl complex responsible for the insertion reaction has not been observed to date.

[25] An alternative mechanism involving initial in situ reduction to a metal(0) complex and formation of a ($\pi$-allyl)metal intermediate can also, in principle, account for the isomerized olefin 7. However, the extreme distortion of the allyl ligand and the geometrically unlikely C–H oxidative addition required by this alternative are highly unlikely.

[26] Preparation of 7: Allan, R. D.; Wells, R. J. *Aust J. Chem.* **1970**, *23*, 1625.



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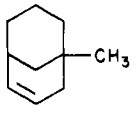

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The greater stability of the platinum–pyridine complex 5 relative to the palladium–nitrile complexes is not fully understood but may be due to the metal (Pt vs. Pd) or the enhanced lability of the nitrile that can more readily create coordinatively unsaturated, reactive species.

We are currently broadening our studies of these complexes to include additional anti-Bredt olefins and metals (Fe, Ir, Rh) as well as further investigations into the reactivity of these unique complexes. In particular, these species are well suited to mechanistic studies of insertions because of their clear propensity to undergo such reactions and because of their inability to participate in competitive processes involving direct ligand attack, and we are focusing additional studies in this area.

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**Registry No.** 3, 17530-61-9; 4, 86508-21-6; 5, 86508-19-2; 6, 86560-60-3; 8, 86508-22-7; 9, 86508-23-8; 14, 86508-24-9; 15, 86508-25-0; (ethylene)$PtCl_2$(pyridine), 12078-66-9; $Pd(OAc)_2$, 3375-31-3; $Pd(CH_3CN)_2Cl_2$, 14592-56-4; $Pd(PhCN)_2Cl_2$, 14220-64-5; $Pd(Me)_2(PPh_3)_2$, 36485-69-5; $Pd(CD_3)_2(PPh_3)_2$, 86508-20-5.

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# Synthesis of Open Metal Carbonyl Cluster Compounds. The Reactions of *closo*-Sulfido Metal Carbonyl Cluster Compounds with $H_2S$. Synthesis and Crystal and Molecular Structure of $H_2Os_5(CO)_{14}(\mu_3\text{-}S)_2$

**Richard D. Adams,* István T. Horváth, and Li-Wu Yang**

*Department of Chemistry, Yale University*
*New Haven, Connecticut 06511*

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*Summary:* The reactions of the *closo*-sulfido osmium carbonyl cluster compounds $Os_4(CO)_{12}(\mu_3\text{-}S)$, I, and $Os_5(CO)_{15}(\mu_4\text{-}S)$, II, with $H_2S$ yield the open cluster compounds $H_2Os_4(CO)_{12}(\mu_3\text{-}S)_2$, III, and $H_2Os_5(CO)_{14}(\mu_3\text{-}S)_2$, IV, in yields of 55% and 94%, respectively. In each reaction one $H_2S$ molecule has been converted into a triply bridging sulfido ligand and two hydride ligands.

The reaction of metal carbonyl cluster compounds with electron pair donors produces usually either ligand substitution or degradation of the cluster via cleavage of the metal–metal bonds.[1-4] However, if the added donor can serve as a bridging ligand, it could help to preserve the integrity of the molecule even in the presence of extensive cleavage of the metal–metal bonds.[5]

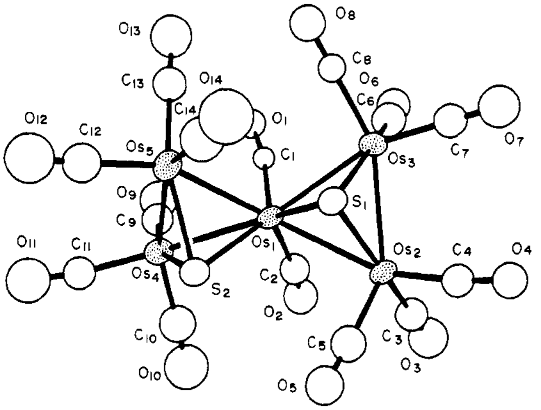
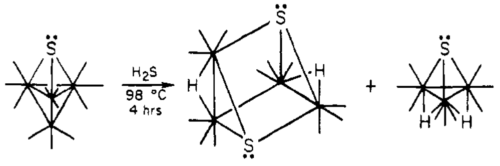


**Figure 1.** An ORTEP plot of $H_2Os_5(CO)_{14}(\mu_3\text{-}S)_2$, IV, showing 50% probability thermal-motion ellipsoids.

The reactions of $H_2S$ with transition-metal complexes often yield complexes containing thiol or sulfido ligands as a result of cleavage of hydrogen–sulfur bonds in the $H_2S$ ligand.[6-10] Sulfido ligands frequently coordinate as bridging, multielectron pair donors.[11] We have now found that the *closo*-sulfido osmium carbonyl clusters $Os_4(CO)_{12}(\mu_3\text{-}S)$, I,[12] and $Os_5(CO)_{15}(\mu_4\text{-}S)$, II,[13] react with $H_2S$ to yield the open disulfido osmium carbonyl clusters $H_2Os_4(CO)_{12}(\mu_3\text{-}S)_2$, III, and $H_2Os_5(CO)_{14}(\mu_3\text{-}S)_2$, IV, respectively.

When refluxed for 4 h in heptane solvent under an atmosphere of $H_2S$, I is converted into the known compounds III and $H_2Os_3(CO)_9(\mu_3\text{-}S)$ in yields of 55% and 35%, respectively.[14] The structure of the selenium analogue of III has been determined previously.[14] The molecule consists of a trigonal prismatic cluster containing four osmium atoms and two sulfido ligands. Hydride ligands bridge two of the three metal–metal bonds. In this addition, the $H_2S$ molecule is converted into one triply bridging sulfido and two bridging hydride ligands. Collectively, these ligands donate six electrons to the cluster. Accordingly, compound I which contains six metal–metal bonds is converted into the open cluster III which contains only three.



I III

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