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# Platinum and Palladium Complexes of Bicyclo[3.3.1]non-1-ene. Bonding and Reactions of Strained Olefin–Transition-Metal Complexes

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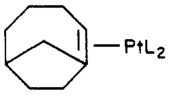
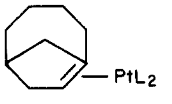
Stable Pt(0) and Pt(II) complexes of bicyclo[3.3.1]non-1-ene have been prepared and exhibit considerable stability relative to the uncomplexed olefin. Despite NMR data indicating significant back-bonding in these complexes, unusually low barriers to rotation around the olefin–metal bond were observed. The substantial metallocyclopropane character ascertained from NMR data apparently translates into greatly enhanced facility for olefin insertion into M–H, M–Cl, and M–R (R = $CH_3$, $CH_2Ph$, allyl) bonds. Possible correlation between the low barrier to rotation and the ability to undergo insertion processes is discussed. The inability of these complexes to undergo ligand attack makes them particularly attractive substrates to study these insertion processes.

## Introduction

The investigation of transition metal–anti-Bredt olefin[1] complexes provides a means of evaluation of a variety of important considerations including the stabilization of the strained bridgehead olefin on complexation and the unusual interaction between a nonplanar $\pi$ system and a transition metal that may translate into the exhibition of novel chemistry from these complexes. On the basis of the bonding scheme employed in understanding the olefin–metal interaction, a reduction of the level of unsaturation ($sp^2 \rightarrow sp^3$) of the olefin takes place on coordination. A comparable rehybridization in a bridgehead olefin may provide substantial stabilization. A number of examples of stabilization of strained unsaturated ligands have been previously reported in the literature including cyclohexyne,[2] benzyne,[3] cyclobutadiene,[4] and bicyclo[2.2.0]hex-1-ene.[5,6] The nonplanar nature of the $\pi$ orbitals of an anti-Bredt olefin, however, presents a unique challenge to the metal not encountered in these earlier cases. The only bridgehead olefin complexes 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]



**1**



**2**

It is known that strained olefins form stronger complexes (larger *K* complexation) than unstrained olefins; e.g., norbornene is a better ligand than cyclopentene.[9] A rough correlation has been shown to exist between $\Delta H$(hydrogenation) and $K$(complexation).[10] This can be understood by consideration of the fact that a strained olefin will benefit more from rehybridization, whether it be by hydrogenation or metal complexation. On the basis of strain arguments, therefore, a bridgehead olefin should be both a better donor and a more willing $\pi$ acceptor. This phenomenon is also revealed by a qualitative representation of the $\pi$ and $\pi^*$ orbitals of a strained bridgehead olefin in comparison with a normal olefin. What is observed, is a compression of the energy difference separating these orbitals. That is, the $\pi$ orbital is not as "bonding" and the $\pi^*$ orbital is not as "antibonding" due to the nonplanar nature of the $\pi$ system. The result of this compression is an energetically more effective overlap of both the olefin $\pi$ and empty $\sigma$ metal orbital and the olefin $\pi^*$ and filled metal d (or hybrid with d symmetry) orbital. This enhanced interaction may be tempered by the nonplanarity of the $\pi$ system, but the diffuse nature of the metal orbitals may prove to be "forgiving" in this interaction. In addition, although these bridgehead systems are trisubstituted olefins that normally are more weakly bound than less substituted olefins, the rigid bicyclic framework will diminish these unfavorable steric interactions. The precise nature of the interaction between the nonplanar $\pi$ system and the metal could be evaluated by spectroscopic characterization and examination of chemical reactivity and contrasted with model-unstrained (olefin)metal complexes. The only reaction reported for **1** and **2** was olefin isomerization.[7,8] In addition, the enhanced ligating ability of these olefins might allow new types of transition-metal monoolefin complexes to be prepared.

In an effort to evaluate these considerations, we have prepared a variety of M(II) and M(0) complexes of Pd and Pt and have characterized them in terms of their bonding and chemical reactivity.[11]

## Results and Discussion

We chose as our prototypal anti-Bredt species bicyclo[3.3.1]non-1-ene (**3**) that was prepared by the pyrolysis of the tetraalkylammonium salt **4** according to the method of Wiseman.[12] In the absence of any metal trapping

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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.

[2] Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750.

[3] Bennett, M. A. "Abstracts of Papers", 185th National Meeting of the American Chemical Society, Seattle, 1983; American Chemical Society: Washington, DC, 1983. McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263.

[4] Fitzpatraick, J. D.; Emerson, G. F.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 3254.

[5] Jason, M. E.; McGinnety, J. A.; Wiberg, K. *J. Am. Chem. Soc.* **1974**, *96*, 6531.

[6] For other examples of transition-metal stabilization of strained olefins, see: Evers, J.; Mackor, A. *Tetrahedron Lett.* **1978**, 2317. Visser, J. P.; Ramakers, J. E. *J. Chem. Soc., Chem. Commun.* **1972**, 178.

[7] Stamm, E.; Becker, K. B.; Engel, P.; Ermer, O.; Keese, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 685.

[8] Stamm, E.; Becker, K. B.; Engel, P.; Keese, R. *Helv. Chim. Acta* **1979**, *62*, 2181. 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: Van Buren, M.; Hanson, H. J. *Helv. Chim. Acta* **1977**, *60*, 2717.

[9] Muhs, M. A.; Weiss, F. T. *J. Am. Chem. Soc.* **1962**, *84*, 4697.

[10] Herberhold, M. "Metal $\pi$ Complexes"; Elsevier: New York, 1974; Vol. II, p 146.

[11] A preliminary account of this work has been published: Godleski, S. A.; Valpey, R. S.; Gundlach, K. B. *Organometallics* **1983**, *2*, 1254.

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

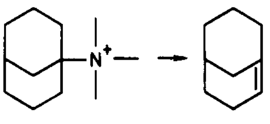
| | |
|---|---|
| 3 | $^{13}$C NMR δ(C(1)) 148.25, δ(C(2)) 125.77 ($J_{C(2)-H}$ = 160.6 Hz); $^1$H NMR 5.72 ppm (H$_a$, t, $J$ = 6.59 Hz) |
| 5 | $^{13}$C NMR δ(C(1)) 120.45 ($J_{Pt-C(1)}$ = 211.6 Hz), δ(C(2)) 84.25 ($J_{Pt-C(2)}$ = 202.9 Hz, $J_{C(2)-H}$ = 159.8 Hz); $^1$H NMR 5.54 (H$_a$, t, $J$ = 7.0 Hz, $J_{Pt-H}$ = 73.3 Hz) |
| 2-methyl-2-butene | $^{13}$C NMR δ(C(1)) 132.0, δ(C(2)) 118.4 ($J_{C(2)-H}$ =151.3 Hz) |
| 6 | $^{13}$C NMR δ(C(1)) 116.01 ($J_{Pt-C(1)}$ = 143.6 Hz, δ(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 room temperature on Bruker WH-400.

Table II. Shift (Ppm) on Complexation to Pt(II) for 3 and 2-Methyl-2-butene

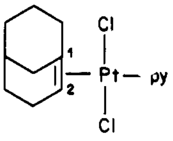
| | 3 | 2-methyl-2-butene |
|---|---|---|
| Δδ(C$_1$) | 27.8 | 14.7 |
| Δδ(C$_2$) | 41.5 | 34.0 |

reagent, the only reaction that 3 undergoes in solution is [2 + 2] dimerization with a $t_{1/2}$ of ~3 days.

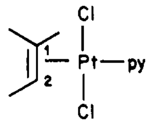


4 3

**Metal(II) Complexes.** Reaction of bicyclo[3.3.1]non-1-ene (3) with ethylene PtCl$_2$(py) in CDCl$_3$ at 0 °C with N$_2$ bubbling through the solution to drive off the ethylene led to efficient olefin exchange producing the [3.3.1] olefin complex 5 in quantitative yield. Spectral characterization of 5 is given in Table I.[13] Included for comparison purposes are data for the model trisubstituted olefin complex of 2-methyl-2-butene (6) as well as data for the uncomplexed olefins. Immediately apparent are anomalously large shifts on complexation for the bridgehead olefin relative to the model complex 6 in the $^{13}$C NMR (Table II) as well as the enhanced $J_{Pt-C}$ coupling constants (Table I). These data indicate a stronger interaction with the metal and more significant rehybridization on complexation and suggest more metallocyclopropane character in the bridgehead olefin complex.



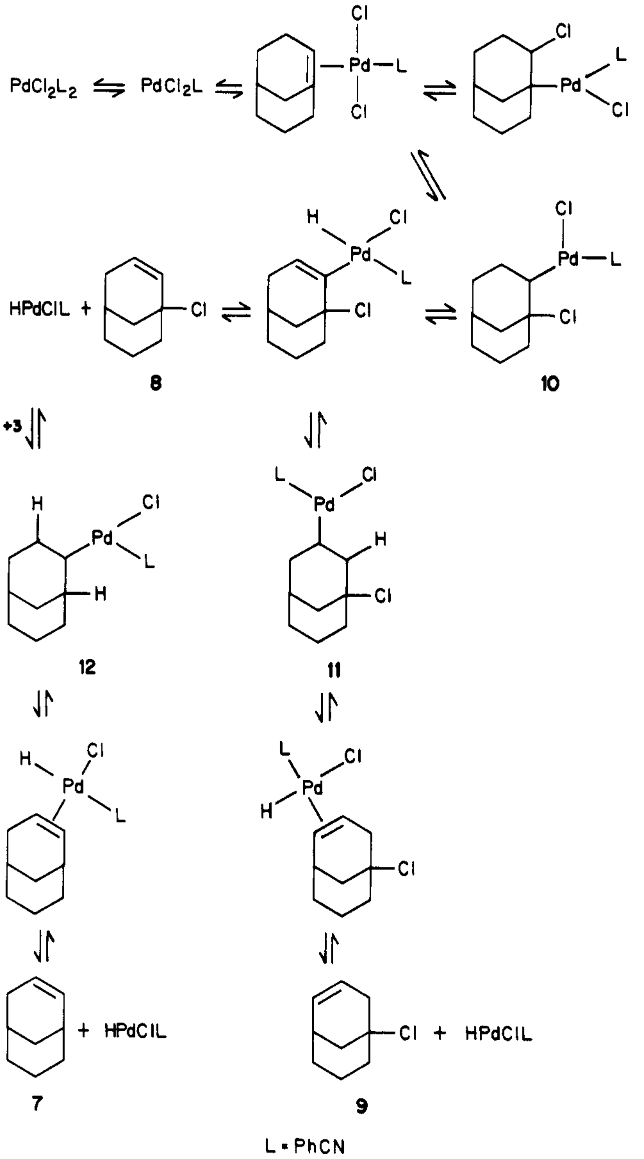
5



6

In addition, a sample of 5 has been kept at room temperature for 6 months and shows no signs of decomposition or dimerization, demonstrating that the predicted stabilization of this species was in fact being fully realized.

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



**Reactions of M(II) Complexes.** Whereas Pt(II) provided a stable complex, Pd(II) compounds exhibited reactions with 3. Admixture of 3 with Pd(OAc)$_2$ (1 equiv, 0.1 M in THF-$d_8$, 5 min, room temperature) provided only the rearranged olefin 7 in quantitative yield. A likely mechanism for this reaction 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 two bridgehead chlorinated olefins 8 and 9 (7:8:9; 2:1:1 ratio, >95% total yield based on $^1$H NMR analysis with an internal standard).[14]

The products of these reactions can be accounted for by the mechanism shown in Scheme I. Complexation of the olefin follows loss of a ligand L. Insertion into Pd–Cl by the olefin can proceed in two regiochemical senses with the σ-bound Pd species 10 being exclusively produced presumably for both steric and electronic reasons. β-Hydride elimination from 10 provides 8 and a Pd–H species. Once a Pd–H moiety is produced, it can hydropalladate 8 to provide 11 wherein β-H elimination will provide 9 or it can compete with the insertion by 3 into Pd–Cl and provide 12 that can β-H eliminate and give the rearranged olefin (7).

We believe this same mechanism is also operating in the case of the Pd(OAc)$_2$ reaction except that after the "initiation event" of Pd–OAc insertion, a Pd–H species is

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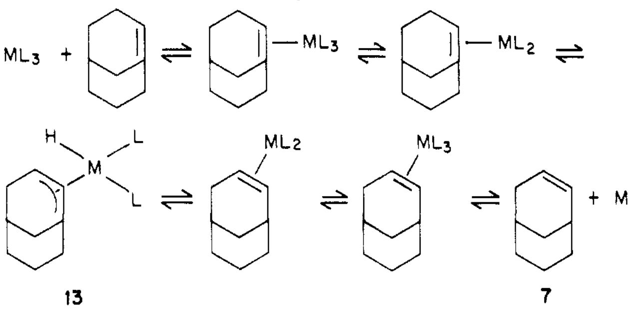
(12) Wiseman, J. R.; Pletcher, W. A. *J. Am. Chem. Soc.* **1979**, *92*, 956.

(13) $^{195}$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.

(14) This ratio differs from the one we initially reported in our preliminary report but appears to be more consistent with our additional experiments with this reaction.

Scheme II. Mechanism for Olefin Isomerization via a $\pi$-Allyl Intermediate



produced that subsequently dominates the reaction providing only **7** as observable product.

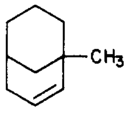
An alternative mechanism for olefin isomerization involving a ($\pi$-allyl)palladium intermediate **13** is shown in Scheme II. This process requires in situ reduction of the Pd(2+) species to Pd(0) to allow for $\pi$-allyl formation via oxidative addition into the allylic C–H bond. This oxidative-addition step appears to be geometrically unfeasible. In addition, the resulting $\pi$-allyl moiety would be significantly nonplanar and severely distorted from its optimal geometry. As a result, we strongly disfavor this mechanism.

The observation of **8** and **9** has added mechanistic significance as the 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 addition via nucleophilic attack by $Cl^-$ on the olefin ligand. Ligand attack of $Cl^-$ on the face opposite the Pd is clearly prohibited in **3**.

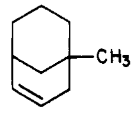
Evidence supporting an insertion mechanism as opposed to a syn addition of $Cl^-$ was provided by the observation that the addition of 3 equiv of tri-*n*-octylmethylammonium chloride to the $Pd(PhCN)_2Cl_2$ reaction mixture produced no increase in the relative amounts of **8** and **9** vs. **7**. Presumably, the rate of a syn addition process would be dependent on the $[Cl^-]$ and this observation indicates that this mechanism is not operating.

In addition, although 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. Furthermore, it should be noted that although substantial amounts of nonbridgehead olefins are produced (**7**–**9**) during the course of this reaction, no products derived from Pd–Cl insertion by these species were ever observed, further documenting the enhanced reactivity of the strained olefin. This facility for Pd–Cl insertion can perhaps be understood on the basis of the information gained from the stable Pt(II) complex **5** that showed enhanced metallocyclopropane character relative to the model complex. The greater $\sigma$ character of the M–C bonds in the analogous Pd complex may be promoting the insertion process. The ability of these olefins to readily assume the preferred geometry for insertion (vide infra) may also be of significance.

The facility of **3** for undergoing insertion reactions was further demonstrated by the following examples. Reaction of **3** with $Pd(CH_3)_2(PPh_3)_2$ (2 equiv, 0.1 M $CDCl_3$, room temperature, 90 min) yielded **7**, **14**, and **15** (5:2:1; >95% total yield based on GC analysis with an internal standard) presumably via a mechanism comparable to that shown in Scheme I but now initiated by insertion of the bridgehead olefin into Pd–Me. When this reaction was repeated by using $Pd(CD_3)_2(PPh_3)_2$, intact incorporation of the $CD_3$ unit at the bridgehead was observed, rendering the possibility of a $Pd{=}CH_2$ ($CD_2$) intermediate unlikely. Although alkyl–metal olefin insertions are believed to be operating in Ziegler–Natta polymerizations,[19] the direct observation of such reactions is relatively rare.[20,21] We are attempting low-temperature NMR studies to allow the direct observation of the presumed olefin–Pd–Me complex and provide more evidence regarding this point.

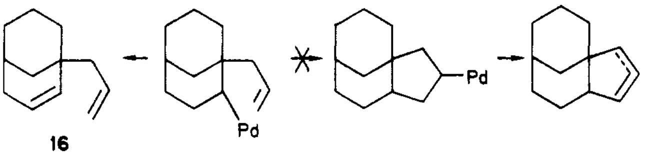


**14**



**15**

On the basis of the apparent ease of insertion and the inability of reactions to proceed by ligand addition in these bicyclic bridgehead olefins, these species appear to be excellent substrates to study the fundamental organometallic process of insertion. In particular, competition experiments as exemplified below could prove informative. Reaction of $Pd(PPh_3)_2(Me)(I)$ in $CDCl_3$ at room temperature gave only **7**, **14**, and **15** (76:9:15) with no bridgehead iodide being detected, whereas admixture of $Pd(\eta^3\text{-allyl})(\eta^5\text{-Cp})$ gave only bridgehead allylated product **16** and rearranged olefin **7** ($CDCl_3$, −10 °C, 24 h, **16**:**7**, 23%:70%). Disappointingly, no fused cyclopentene products were produced in the latter reaction.



**16**

**Olefin Rotation.** Rotation of olefins around the metal–carbon bond has been demonstrated in a number of complexes.[23] A simple orbital analysis of the electronic component of this rotation process reveals that the $\sigma$ bond between a filled olefin $\pi$ orbital and an unfilled $\sigma$ hybrid metal orbital is insensitive to the rotation process, whereas the $\pi$ interaction, which is comprised of a $\pi^*$ orbital on the ligand and a filled metal d (or hybrid with d symmetry)

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[15] Evidence suggesting cis chloropalladation of olefins has been provided in: Henry, P. M. *J. Org. Chem.* **1976**, *37*, 2443. 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 Leuvwen, P. W. N.; 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.

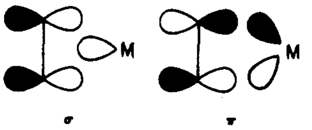
[19] Proposal of Ziegler–Natta polymerization proceeding by alkyl-metal–olefin insertion: Henrici-Olive, G.; Olive, S. *Top. Curr. Chem.* **1976**, *67*, 107. Thorn, D. L.; Hoffman, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079. Heck, R. F. *Ibid.* **1968**, *90*, 5518. Cooke, M. P., Jr.; Parlman, R. 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.

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

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

[22] 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, 1971; 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 an olefin into a ($\sigma$-aryl)palladium complex but functions only for aryl, heterocyclic, vinyl, and benzyl species bound to the metal; see: Heck, R. F. *Pure Appl. Chem.* **1978**, *60*, 691.

[23] Cramer, R. *J. Am. Chem. Soc.* **1964**, *86*, 217.



orbital, is perturbed by rotation. A 0° dihedral angle between these orbitals represents one energy minimum with a second minimum expected to exist at a 90° rotation at which point a second d orbital on the metal can interact effectively with the $\pi^*$ orbital. The maximum in electronic energy in the rotation process should occur at a 45° dihedral angle.

Superimposed on these electronic considerations are factors associated with the steric interactions during the rotation between the olefin and the ligands disposed cis to it. When applied to square-planar $d^8$ $ML_3$–olefin complexes, it has been convincingly argued from both theoretical[24] and experimental work[25] that these steric factors generally dominate the overall energetics of the rotation barrier defining the 90° (perpendicular to square-planar orientation) as the minimum and the 0° orientation (in plane coordination) as the geometry associated with the maximum in energy.

Despite the dominance of steric effects, electronic influences on $\Delta G^*$ rotation have been evidenced in $d^8$ complexes of Rh.[26] In general, the degree of back-bonding ($d \rightarrow \pi^*$) exhibited in a complex will be translated into changes in the barrier to rotation around the metal–olefin bond, with greater degrees of back-bonding giving rise to higher barriers to rotation.

On the basis of the $^{13}C$ NMR data (shift on complexation) considerably greater back-bonding exists in the $Pt^{II}Cl_2(py)$ complex **5** relative to the model 2-methyl-2-butene system (**6**) and a relatively high rotation barrier could be anticipated. However, the [3.3.1] olefin should be considerably less sterically demanding than a normal trisubstituted olefin, suggesting a low rotation barrier.

To evaluate the degree of back-bonding and steric influences as well as generally further contrast the anti-Bredt olefin complex with normal olefin species, variable-temperature $^1H$ NMR studies were undertaken employing a Pt (acac)Cl(olefin) complex. Typical $\Delta G^*$ rotation values that have been obtained previously were in the 8–15 kcal/mol range making NMR analysis particularly convenient. This complex was chosen because its inherent asymmetry allows the formation of diastereomeric complexes with unsymmetrical olefins at the cessation of rotation and because extensive work with simple olefins had already been completed and was available for comparison.[25] The complexes of **3** and 2-methyl-2-butene were prepared by simple exchange with the corresponding ethylene compound. Summary of the data obtained is included in Table III. Surprisingly, the coalescence temperature of the Pt(II) complex of **3** at 400 MHz in $CDCl_3$ was 233 ± 5 K whereas the corresponding model trisubstituted complex of 2-methyl-2-butene exhibited a coalescence temperature of 298 ± 5 K. In both cases approximately 4:1 ratios of diasteromeric complexes were observed below coalescence, and Pt–H couplings were seen at fast rotation, indicating that no intermolecular exchange processes were operating. Employing the exact process used in the previous studies[25] approximate $\Delta G^*$ rotation values were calculated on the basis of the equation

$$\Delta G^*_T = -RT \ln (\pi \Delta \nu h / (2)^{1/2} kT)$$

where $T$ = coalescence temperature and $\Delta\nu$ = separation in hertz of resonances of diastereomers in absence of exchange.

The low barrier of rotation exhibited by the complex of **3** (10.7 kcal/mol) relative to 2-methyl-2-butene (14.7 kcal/mol) can readily be ascribed to the diminished steric interactions by the rigid bicyclic system in the in-plane geometry overriding the significant degree of back-bonding. The observation that the rotation barrier in the complex of **3** is less than even ethylene (12.7 kcal/mol), however, remains puzzling, as it is difficult to imagine **3** being less sterically demanding than $C_2H_4$. There exists the intriguing possibility that the nonplanar nature of the olefin may be influencing the nature of the barrier to rotation.[27]

The easy access to the in-plane coordinated geometry that is predicted[28] to be the preferred geometry for insertion processes may explain the enhanced ability of the complexes of **3** to undergo this reaction.

**Metal(0) Complexes.** Reaction of $Pt(PPh_3)_2$(ethylene) with bicyclo[3.3.1]non-1-ene (**3**) (1 equiv) at −30→0 °C in $CH_2Cl_2$ ($N_2$ bubbled through to drive off ethylene) provided after 20 min a 95% yield of the Pt(0) complex **17**. Complete spectroscopic characterization of **17** including $^1H$, $^{13}C$, and $^{31}P$ NMR is given in Table IV. Added for comparison is data for the $Pt(PPh_3)_2$(ethylene) complex. The use of this model system is somewhat unfair as ethylene typically shows the largest shifts on complexation and coupling constants to Pt; however, the corresponding 2-methyl-2-butene species could not be prepared. This result further suggests that the bridgehead olefin **3** may possess enhanced ligating ability relative to a nonstrained trisubstituted olefin. The $^{13}C$ NMR data are again most revealing showing abnormally large $J_{Pt-C}$ and $\Delta\delta(C)$ complexation values comparable to the ethylene complex which is most unusual for a trisubstituted olefin.

Once again stable Pd complexes of **3** could not be prepared.

**Reactions of M(0) Complexes.** Reaction of the $Pt(PPh_3)_2$ complex **17** with $CH_3I$ (4–5 equiv, $CDCl_3$, room temperature, 15 min) produced a mixture of bridgehead methylated olefins **14** and **15** in addition to the rearranged olefin **7** in a ratio of **14**:**15**:**7** of 4:1:32, presumably by a mechanism involving oxidative addition to Pt by $CH_3I$ followed by insertion of Pt–Me and β-H elimination and the ensuing steps shown in Scheme I.

Although isolable Pd(0) complexes could not be prepared, mixture of bis(triphenylphosphine)(ethylene)$Pd^0$ (1 equiv), **3** (1 equiv) and $CH_3I$ (2 equiv) in $CDCl_3$ at room temperature produced in 20 min a 97:3 ratio of **7**:**14** + **15** with **15** predominating. Comparable reaction with benzyl bromide (5 equiv) in $CDCl_3$ at room temperature yielded **7** and bridgehead benzylated species **18** and **19** in a **7**:**18**:**19** (15:5:1) ratio. The greater efficiency of oxidative addition by $PhCH_2Br$ relative to $CH_3I$ may explain the increased yield of bridgehead alkylated products in this case. Trace quantities of a compound tentatively identified as the product of Pd–$CH_2Ph$ insertion into **7** followed by β-H elimination were also observed.

Once again, although substantial amounts of nonbridgehead olefins were produced during the course of these reactions, no significant amounts of products derived from

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(24) Albright, T. A.; Hoffman, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801 and references therein.

(25) Holloway, C. E.; Hulley, G.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. A* **1969**, 53; **1970**, 1653.

(26) Cramer, R.; Kline, J. B.; Roberts, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 2519.

(27) The in-plane geometry may be sufficiently low in energy so as to lose its position as the maximum in energy to some intermediate in rotation angle (~45°). The greater ability to the twisted olefin to maintain overlap with the appropriate d orbitals throughout the rotation may be involved.

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**Table III. Coalescence Temperatures and Barriers to Rotation**

| olefin | $\Delta\nu$,[a] Hz | $T$(coalescence), K | NMR field strength, MHz | $\Delta G^{\ddagger}{}_{T}$, kcal/mol | ref |
|---|---|---|---|---|---|
| ethylene | 24.5 | 253 ± 3 | 100 | 12.7 | 25 |
| propene | 23.0 | 255 ± 5 | 100 | 12.8 | 25 |
| *cis*-2-butene | 15 ± 2 | 253 ± 5 | 100 | 13.0 | 25 |
| *trans*-2-butene | 25.5 | 329 | 100 | 16.1 | this work |
| **3** | 183.6 | 233 ± 5 | 400 | 10.7 | this work |
| 2-methyl-2-butene | 158.2 | 298 ± 5 | 400 | 14.0 | |

[a] $\Delta\nu$ = separation of resonances in absence of exchange.

**Table IV. NMR Data for $Pt(PPh_3)_2$(ethylene) and 17**

| | | |
|---|---|---|
| 17 | $^1H$ NMR | $\delta(H_a)$ 2.22 ($\Delta\delta$(H) complexation = 3.51 ppm) |
| | | $J_{H-H}$ = 7.3 Hz, $J_{Pt-H}$ = 61.5 Hz |
| | $^{13}C$ NMR | $C_1$ 61.4 ppm ($\Delta\delta$(C1) complexation = 86.6 ppm) |
| | | $J_{Pt-C1}$ = 320 Hz, $J_{C1-P}$ = 43.14 Hz |
| | | $\delta$(C2) 52.5 ($\Delta\delta$(C2) complexation = 73.5 ppm) |
| | | $J_{Pt-C2}$ = 220 Hz, $J_{C2-H}$ = 147.0 Hz, $J_{C2-P}$ = 43.15 Hz |
| | $^{31}P$ NMR | $\delta$(P) trans 31.6 |
| | | $J_{Pt-P}$ = 1528 Hz, $J_{P-P}$ = 50.2 Hz |
| | | $\delta$(P) cis 30.5 |
| | | $J_{Pt-P}$ = 1224 Hz, $J_{P-P}$ = 50.2 Hz |
| (ethylene)$Pt(PPh_3)_2$ | $^1H$ NMR | H 2.16 ppm ($\Delta\delta$(H) complexation = 3.28 ppm) |
| | | $J_{Pt-H}$ = 60.1 Hz |
| | $^{13}C$ NMR | $\delta$(C) 39.6 ($\Delta\delta$(C)) = 88 ppm) |
| | | $J_{Pt-C}$ = 194 Hz |

their reactions with Pd–R or Pt–R were ever observed.

## Conclusions

Stable Pt(0) and Pt(II) complexes of bicyclo[3.3.1]non-1-ene have been prepared demonstrating the ability of transition metals to effectively interact with and stabilize strained bridgehead olefins. Spectroscopic characterization of these species revealed substantial rehybridization of the olefin on complexation based on $\Delta\delta$(C) (complexation) in the $^{13}C$ NMR and significant $\sigma$ character in the M–C bonds based on Pt-C coupling constants relative to model olefin complexes.

Unusually low barriers to rotation around the olefin–metal bond were observed relative to model systems, particularly in light of the degree of back-bonding determined from the NMR data.

The Pd(II) species show a remarkable facility for undergoing insertion reactions of Pt–H, Pd–R, and Pd–Cl bonds, presumably due to the enhanced $\sigma$ character in the M–C bonds and/or because of their ability to assume in-plane coordination. Because of the inability of these species to undergo ligand attack, they appear to be extremely attractive targets for study of these insertion processes.

Currently, we are examining complexes of **3** that have been prepared from Cr, W, Mo, and Fe carbonyls.

## Experimental Section

**General Data.** All of the NMR studies ($^1H$, $^{13}C$, $^{31}P$) including variable-temperature runs were performed on a Bruker WH-400 NMR. Chemical shifts are reported in parts per million relative to the internal standards $Me_4Si$ (0.0 ppm) or $CHCl_3$ (7.24 ppm). Multiplicities are expressed as s, singlet, d, doublet, t, triplet, q, quartet, b, broad, and m, multiplet. Coupling constants are listed in hertz. Analytical GLC was obtained on a Perkin-Elmer 900 equipped with a flame ionization detector. A 6 ft × $^1/_8$ in. 20% SE-30 on Chromosorb W was used for all analytical studies. Peak areas were determined by triangulation. Preparative GLC was accomplished with a Hewlett-Packard 5700A equipped with a thermal conductivity detector. All preparative work was carried out by using a 8 ft × $^1/_4$ in. 20% SE-30 on Chromosorb W column except for the bridgehead olefin **3** that was purified by using a 8 ft × $^1/_4$ in. 15% Carbowax and 4% KOH on Chromosorb W column. GC–MS were performed on a Hewlett-Packard 5990A equipped with a 3 ft × 2 mm 3% Dexsil 400 on 100/200 mesh supelcoprat column. $CDCl_3$ was purified by filtration through alumina immediately before use. THF was purified by distillation from sodium benzophenone ketyl. $CH_2Cl_2$ was distilled from $CaH_2$. Analytical data was obtained from Galbraith, Knoxville, TN.

**Bicyclo[3.3.1]non-1-ene (3).** The bridgehead olefin **3** was prepared by pyrolysis of the ammonium salt **4** and purified by preparative GLC according to the method of Wiseman:[12] $^1H$ NMR ($CDCl_3$) $\delta$ 5.73 (t, $J$ = 7.5 Hz, 1 H), 2.56 (b s, 1 H), 2.30 (m, 1 H), 2.20 (m, 1 H), 2.16 (m, 1 H), 2.02 (m, 1 H), 1.91 (m, 2 H), 1.81 (m, 2 H), 1.50 (m, 1 H), 1.44 (m, 1 H), 1.00 (m, 2 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 148.0 (s, 1 C), 126.0 (d, $J$ = 161.6 Hz, 1 C), 37.1 (t, $J$ = 130.0 Hz, 1 C), 36.7 (d, $J$ = 133.0 Hz, 1 C), 35.3 (t, $J$ = 133.5 Hz, 1 C), 32.4 (t, $J$ = 127.0 Hz, 1 C), 32.0 (t, $J$ = 122.8 Hz, 1 C), 30.7 (t, $J$ = 133.7 Hz, 1 C), 25.8 (t, $J$ = 129.9 Hz, 1 C).

**$Pt(Cl)_2$(py)(bicyclo[3.3.1]non-1-ene) (5).** The $Pt(Cl)_2(py)(C_2H_4)$ complex[29] (0.037 g, 0.08 mmol) was added to a $CDCl_3$ (0.5-mL) solution, cooled to 0 °C which contained **3** (0.01 g, 0.082 mmol). The solution was stirred at 0 °C as $N_2$ was bubbled through for 15 min. The product was then analyzed by $^1H$ NMR which indicated complete exchange had been effected. The solvent was removed under reduced pressure to yield an amorphous yellow solid: decomp pt 144–145 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 8.80 (d, $J$ = 6.5 Hz, 2 H), 7.83 (t, t, $J$ = 6.5, 2.0 Hz, 1 H), 7.43 (t, $J$ = 6.5 Hz, 2 H), 5.54 (d, t, $J_{Pt-H}$ = 73.3, $J_{H-H}$ = 7.0 Hz, 1 H), 2.82 (m, 2 H), 2.56 (b s, 1 H), 2.46 (m, 1 H), 2.37 (m, 1 H), 2.25 (d, $J$ = 13.5 Hz, 1 H), 2.02 (m, 2 H), 1.89 (m, 1 H), 1.62 (m, 1 H), 1.55 (m, 1 H), 1.28 (m, 1 H), 1.11 (m, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 152.0 (d, $J$ = 187 Hz, 2 C), 139 (d, $J$ = 164 Hz, 1 C), 125 (d, $J$ = 169 Hz, 2 C), 120.5 ($J_{Pt-C}$ = 211.6 Hz, 1 C), 84.3 (d, d, $J_{Pt-C}$ = 202.9, $J_{C-H}$ = 159.8 Hz, 1 C), 41.4 (t, $J$ = 144 Hz, 1 C), 39.8 (t, $J$ = 134 Hz, 1 C), 37.7 (d, $J$ = 139 Hz, 1 C), 32.6 (t, $J$ = 97 Hz, 1 C), 28.0 (t, $J$ = 129 Hz, 2 C), 31.5 (t, $J$ = 96 Hz, 1 C). Anal. Calcd for $C_{14}H_{19}NCl_2Pt$: C, 35.98; H, 4.10. Found: C, 35.81; H, 4.10.

**$Pt(Cl)_2$(py)(2-methyl-2-butene) (6).** The $Pt(Cl)_2(py)(C_2H_4)$[29] complex (0.121 g, 0.325 mmol) was dissolved in $CHCl_3$ (5.0 mL) at room temperature, and 2-methyl-2-butene (5.0 g, 7.1 mmol) was added. The solution was stirred at 25 °C with $N_2$ bubbling through for 30 min. The solution was then cooled, and the solvent and excess olefin were removed to give an amorphous yellow solid: $^1H$ NMR ($CDCl_3$) $\delta$ 8.79 (d, $J$ = 7.0 Hz, 2 H), 7.80 (t, $J$ = 7.0 Hz, 1 H), 7.40 (t, $J$ = 7.0 Hz, 2 H), 5.63 (d, q, $J_{Pt-H}$ = 66.0 Hz, $J_{H-H}$ = 6.0 Hz, 1 H), 2.07 (s, 3 H), 1.83 (s, 3 H), 1.81 (d, $J$ = 6.0 Hz, 3 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 151.9 (d, $J$ = 181.7 Hz, 2 C), 139.1 (d, $J$ = 168.7 Hz, 1 C), 125.1 (d, $J$ = 168.7 Hz, 2 C), 116.0 ($J_{Pt-C}$ = 143.6 Hz, 1 C), 84.7 (d, d, $J_{Pt-C}$ = 147.2 Hz, $J_{C-H}$ = 154.4 Hz, 1

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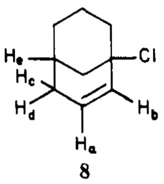
C), 30.3 (q, $J$ = 125.7 Hz, 1 C), 23.9 (q, $J$ = 125.7 Hz, 1 C), 17.0 (q, $J$ = 125.7 Hz, 1 C).

**Pt(Cl)(acac)(bicyclo[3.3.1]non-1-ene).** Pt(Cl)(acac)(ethylene)[30] (0.0179 g, 0.05 mmol) was added to a $CDCl_3$ (1 mL) solution of bicyclo[3.3.1]non-1-ene (3) (0.0059 g, 0.048 mmol). The stirring solution was cooled to 0 °C, $N_2$ was bubbled through for 25 min, and then the solution was warmed to room temperature for 15 min. The reaction mixture was then recooled as solvent was removed in vacuo. Trituration of the resulting material with pentane gave a light yellow solid (0.023 g, 97%): $^1$H NMR ($CDCl_3$) (25 °C) δ 5.44 (s, 1 H), 5.17 (d, t, $J_{\text{Pt-H}}$ = 71 Hz, $J_{\text{H-H}}$ = 7.1 Hz, 1 H), 2.48 (b s, 1 H), 2.40 (m, 2 H), 2.24 (m, 2 H), 2.11 (m, 1 H), 2.08 (s, 3 H), 1.97 (m, 1 H), 1.88 (s, 3 H), 1.58 (m, 4 H), 1.20 (m, 1 H), 1.15 (m, 1 H); $^1$H NMR ($CDCl_3$) (−65 °C) δ 5.27 (b m, $^4/_5$ H), 4.81 (b m, $^1/_5$ H); $^{195}$Pt satellites were too broad to detect; $^{13}$C NMR ($CDCl_3$) (25 °C) δ 185.8 ($J_{\text{Pt-C}}$ = 62.3 Hz), 184.3 ($J_{\text{Pt-C}}$ = 51.3 Hz), 106.8 ($J_{\text{Pt-C}}$ = 266.1 Hz), 100.5 ($J_{\text{C-H}}$ = 163.5 Hz, $J_{\text{Pt-C}}$ = 63.5 Hz), 76.6 ($J_{\text{Pt-C}}$ = 256.4 Hz), 37.7 ($J_{\text{C-H}}$ = 136.7 Hz), 37.6 ($J_{\text{C-H}}$ = 136.7 Hz), 35.7 ($J_{\text{C-H}}$ = 134.2 Hz), 32.4 ($J_{\text{C-H}}$ = 127.0 Hz), 29.7 ($J_{\text{Pt-C}}$ = 31.7 Hz, $J_{\text{C-H}}$ = 124.4 Hz), 28.6 ($J_{\text{Pt-C}}$ = 36.7 Hz, $J_{\text{C-H}}$ = 125.7 Hz), 26.6 ($J_{\text{C-H}}$ = 128.0 Hz), 26.2 ($J_{\text{C-H}}$ = 131 Hz), 25.2 ($J_{\text{C-H}}$ = 131.8 Hz).

**Pt(Cl)(acac)(2-methyl-2-butene).** Pt(Cl)(acac)(ethylene)[30] (0.034 g, 0.095 mmol) and 2-methyl-2-butene (1.5 g, 21.4 mmol) were dissolved in 0.5 mL of $CH_2Cl_2$. $N_2$ was bubbled through the solution for 30 min at room temperature. The solution was then cooled to 0 °C, and solvent and excess olefin were removed at reduced pressure, yielding 0.036 g (95%) of the desired complex: $^1$H NMR ($CDCl_3$) major isomer (80%) (−60 °C) δ 5.48 (s, 1 H), 5.33 (d, q, $J_{\text{Pt-H}}$ = 65 Hz, $J_{\text{Pt-H}}$ = 7.3 Hz, 1 H), 2.03 (s, 3 H), 1.89 (s, 3 H), 1.84 (d, $J_{\text{Pt-H}}$ = 40.5 Hz, 3 H), 1.49 (d, $J$ = 7.3 Hz, 3 H), 1.40 (d, $J_{\text{Pt-H}}$ = 39.6 Hz, 3 H); minor isomer (20%) δ 5.48 (s, 1 H), 4.93 (d, q, $J_{\text{Pt-H}}$ = 65 Hz, $J_{\text{Pt-H}}$ = 7.3 Hz, 1 H), 2.03 (s, 1 H), 1.89 (s, 3 H), 1.73 (s, 3 H), 1.70 (d, $J$ = 7.3 Hz, 1 H), 1.60 (s, 3 H); $^1$H NMR (85 °C) δ 5.24 ($J_{\text{Pt-H}}$ = 70.7 Hz, $J_{\text{H-H}}$ = 6.35 Hz).

**Reaction of 3 with $PdCl_2(PhCN)_2$.** Bicyclo[3.3.1]non-1-ene (3) (0.005 g, 0.041 mmol) and $Pd(Cl)_2(PhCN)_2$ (0.015 g, 0.2 mmol) were dissolved in 0.5 mL of $CDCl_3$ at room temperature. $^1$H NMR analysis after 10 min with an internal integration standard ($Et_2O$) indicated at 2:1:1 mixture of 7:8:9. The isomerized olefin 7 was purified by preparative GLC and spectrally compared with an authentic sample prepared by the method of Allan[30] and found to be identical in all respects: $^1$H NMR ($CDCl_3$) δ 5.81 (d, t, $J$ = 10.0, 3.2 Hz, 1 H), 5.65 (t, $J$ = 10.0 Hz, 1 H), 2.32 (d, d, $J$ = 18, 7 Hz), 2.21 (b s, 1 H), 2.21 (b s, 1 H), 1.98 (t, $J$ = 4 Hz, 1 H), 1.82 (d, d, $J$ = 18, 3 Hz, 1 H), 1.63 (m, 1 H), 1.54 (m, 4 H), 1.43 (m, 2 H), 1.37 (m, 1 H). Anal. Calcd for $C_9H_{14}$: C, 88.45; H, 11.55. Found: C, 88.23; H, 11.34. 8 and 9 were collected by preparative GLC (mixture not separated) and characterized by $^1$H NMR ($CDCl_3$) and GC–MS: $^1$H NMR (8) δ 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 ($H_e$, t, $J$ = 3 Hz), 2.12 (m, 1 H), 1.94 (m, 1 H), 1.68 (m, 1 H), 1.55 (m, 4 H), 1.39 (m, 1 H); $^1$H NMR (9) δ 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 ($H_e$, d, d, $J$ = 18, 3 Hz), 2.25 (m, 1 H), 2.10 (m, 1 H), 2.00 (m, 1 H), 1.91 (m, 1 H), 1.59 (m, 1 H), 1.53 (m, 2 H), 1.40 (m, 1 H); MS $m/e$ 158, 156, 115, 113; high-resolution MS, $m/e$ 156.6599 (calcd), 156.6586 (found). Anal. Calcd for $C_9H_{13}Cl$: C, 69.00; H, 8.37. Found: C, 69.40; H, 8.26.



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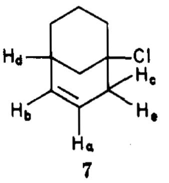
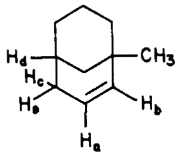


7

**Reaction of 3 with $Pd(Me)_2(PPh_3)_2$.** Reaction of 3 (0.006 g, 0.048 mmol) with $Pd(Me)_2(PPh_3)_2$[31,32] (0.054 g, 0.082 mmol) in $CDCl_3$ (0.6 mL) for 90 min at room temperature followed by $^1$H NMR analysis with $Et_2O$ as an internal standard produced a 5:2:1 ratio of 7:14:15. Reaction with $Pd(CD_3)_2(PPh_3)_2$[31,32] under identical conditions provided the methylated products in similar ratios but with no H incorporation at the methyl group. The bridgehead methylated compounds 14 and 15 were collected by preparative GLC (mixture not separable) and characterized by $^1$H NMR ($CDCl_3$) and GC–MS: $^1$H NMR (14) δ 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 ($H_d$, b t, $J$ = 7 Hz), 1.73 ($H_e$, d, d, t, $J$ = 16, 3, 1 Hz), 1.50 (m, 2 H), 1.45 (m, 1 H), 1.41 (m, 1 H), 1.39 (m, 1 H), 1.32 (m, 1 H), 1.23 (m, 1 H), 1.12 (m, 1 H), 0.91 ($CH_3$, s); $^1$H NMR (15) δ 5.75 ($H_a$, d, t, $J$ = 9, 3 Hz), 5.60 ($H_b$, d, b t, $J$ = 9, 2 Hz), 2.28 ($H_c$, b t, $J$ = 8 Hz), 1.90 ($H_d$, d, d, d, $J$ = 15, 3, 1 Hz), 1.78 ($H_e$, d, d, d, $J$ = 15, 3, 2 Hz), 1.48 (m, 2 H), 1.45 (m, 2 H), 1.38 (m, 2 H), 1.35 (m, 1 H), 1.15 (m, 1 H), 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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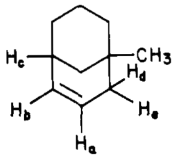

15

**Reaction of with *cis*-$Pd(PPh_3)_2(Me)(I)$.** The bridgehead olefin 3 (0.0025 g, 0.02 mmol) and *cis*-$Pd(PPh_3)_2(Me)(I)$[33] (0.046 g, 0.06 mmol) were dissolved in $CDCl_3$ (0.5 mL) and reacted for 10 min prior to $^1$H NMR analysis. The products that were formed were 7, 14, and 15 in a ratio of 76:9:15.

**Reaction of 3 with $Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)$.** The bridgehead olefin 3 (0.0033 g, 0.027 mmol) and $Pd(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)$[34] (0.026 g, 0.121 mmol) were dissolved in $CDCl_3$ at −10 °C and maintained at this temperature for 24 h. $^1$H NMR analysis with an internal standard revealed two products 7 (70%) and 1-allylbicyclo[3.3.1]non-2-ene (16) (23%). The bridgehead allylated product was isolated by preparative GLC and analyzed by GC–MS: $^1$H NMR ($CDCl_3$) δ 5.82 (d, t, $J$ = 9.9, 3.3 Hz, 1 H), 5.81 (d, d, t, $J$ = 16.5, 10.6, 8.1 Hz, 1 H), 5.36 (d, d, d, $J$ = 9.9, 4.1, 2.2 Hz, 1 H), 5.00 (d, $J$ = 10.6 Hz, 1 H), 4.99 (d, $J$ = 16.5 Hz, 1 H), 2.25 (d, d, $J$ = 18.6, 7.0 Hz, 1 H), 2.06 (b m, 1 H), 2.04 (d, d, $J$ = 13.5, 8.1 Hz, 1 H), 1.98 (d, d, $J$ = 13.5, 8.1 Hz), 1.74 (d, $J$ = 18.6 Hz, 1 H), 1.52 (m, 3 H), 1.41 (d, $J$ = 11.9 Hz, 1 H), 1.42 (m, 1 H), 1.29 (b m, $J$ = 11.9 Hz, 1 H), 1.23 (m, 2 H); GC–MS, $m/e$ $M^+$ 162.

**$Pt(PPh_3)_2$(bicyclo[3.3.1]non-1-ene).** $Pt(PPh_3)_2$(ethylene)[7,8] (0.137 g, 0.18 mmol) was cooled to −30 °C under $N_2$, and 3 (0.025 g, 0.19 mmol) dissolved in 1.5 mL of $CH_2Cl_2$ was slowly added. The solution was allowed to warm slowly (20 min) to 0 °C while $N_2$ was bubbled through the reaction mixture. Solvent was removed at 0 °C at reduced pressure, yielding 17 as a white solid (0.16 g, 98%): $^1$H NMR ($CDCl_3$) δ 7.25 (m, 15 H), 7.12 (m, 15 H), 2.22 (d, t, $J_{\text{Pt-H}}$ = 64.0 Hz, $J_{\text{H-H}}$ = 7.3 Hz, 1 H), 1.98 (b s, 1 H), 1.72 (b m, 1 H), 1.51 (b m, 2 H), 1.45 (b m, 2 H), 1.32 (m, 2 H), 1.26 (m, 2 H), 1.20 (m, 1 H), 1.13 (m, 1 H), 1.03 (m, 1 H); $^{13}$C NMR ($CDCl_3$) δ 138.2 (d, $J_{\text{C-P}}$ = 34.5 Hz, 6 C), 133.6 (d, $J_{\text{C-H}}$ = 164 Hz, 12 C), 128.6 (d, $J_{\text{C-H}}$ = 152 Hz, 6 C), 127.5 (d, $J_{\text{C-H}}$ = 158 Hz, 12 C), 61.4 (d, d, $J_{\text{Pt-C}}$ = 320 Hz, $J_{\text{C-P}}$ = 43.1 Hz, 1 C), 52.5 (d, d, d, $J_{\text{Pt-C}}$ = 220.5 Hz, $J_{\text{P-C}}$ = 43.1 Hz, $J_{\text{C-H}}$ = 147.0 Hz, 1 C), 38.1 (t, $J_{\text{C-H}}$ = 121 Hz, 1 C), 37.2 (t, $J_{\text{C-H}}$ = 124 Hz, 1 C), 34.4 (t, $J_{\text{C-H}}$ = 112 Hz, 1 C), 32.4 (d, $J_{\text{C-H}}$ = 135 Hz, 1 C); $^{31}$P NMR ($CDCl_3$) δ 31.6 (d, d, $J_{\text{P-P}}$ = 50.2 Hz, $J_{\text{P-Pt}}$ = 1528 Hz), 30.45 (d, d, $J_{\text{P-P}}$ = 50.2 Hz, $J_{\text{P-Pt}}$ = 1224 Hz).

**Reaction of 17 with MeI.** $Pt(PPh_3)$(bicyclo[3.3.1]non-1-ene) (17) (0.02 g, 0.024 mmol) and $CH_3I$ (0.014 g, 0.095 mmol) were reacted in $CDCl_3$ (0.05 mL) at 25 °C for 15 min. $^1$H NMR analysis indicated three products 7, 14, and 15 in a 32:4:1 ratio.

**Reaction of 3 with $Pd(PPh_3)_2(C_2H_4)$ and MeI.** To a $CDCl_3$ solution (0.5 mL) of 3 (0.0031 g, 0.025 mmol) and $Pd(PPh_3)_2(C_2H_4)$[35] (0.013 g, 0.02 mmol) at room temperature was added $CH_3I$ (0.013 g, 0.092 mmol). The reaction was complete after 20 min

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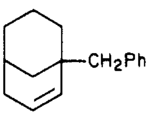
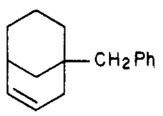
with products and ratios determined by $^1$H NMR. The ratio of 7 to 14 and 15 was 97:3 with the ratio of 15:14 5:1.

**Reaction of 3 with $Pd(PPh_3)_2(C_2H_4)$ and Benzyl Bromide.** The bridgehead olefin 3 (0.004 g, 0.031 mmol), $Pd(PPh_3)_2(C_2H_4)$,[35] and benzyl bromide (0.028 g, 0.17 mmol) were mixed in 0.5 mL of $CDCl_3$ at room temperature. $^1$H NMR analysis after 20 min revealed 7 and two bridgehead benzylated products 18 and 19



**18**



**19**

in a 7:18:19 ratio of 15:1:3. 18 and 19 were isolated by preparative GLC and characterized by $^1$H NMR and MS as a 1:5 mixture, respectively. 18: $^1$H NMR $\delta$ 7.24 (t, $J$ = 6.3 Hz, 2 H), 7.17 (d, $J$ = 6.3 Hz, 2 H), 7.12 (t, $J$ = 6.3 Hz, 1 H), 5.80 (d, t, $J_d$ = 9.7 Hz, $J_t$ = 3.9 Hz, 1 H), 5.48 (d, $J$ = 9.7 Hz, 1 H), 2.64 (d, $J$ = 13.1 Hz, 1 H), 2.53 (d, $J$ = 13.1 Hz, 1 H), 2.21 (b s, 1 H), 2.06 (d, $J$ = 15.0 Hz, 1 H), 1.76 (d, $J$ = 15.0 Hz, 1 H), 1.64 (m, 2 H), 1.39 (m, 4 H), 1.25 (m, 1 H), 1.20 (m, 1 H); MS $m/e$ M$^+$ 212.1. 19: $^1$H NMR ($CDCl_3$) $\delta$ 7.23 (t, $J$ = 6.3 Hz, 2 H), 7.10 (t, $J$ = 6.3 Hz, 1 H), 7.08 (d, $J$ = 6.3 Hz, 2 H), 5.79 (d, t, $J_d$ = 9.6, $J_t$ = 3.4 Hz, 1 H), 5.60 (b t, $J$ = 8.7 Hz, 1 H), 2.49 (d, $J$ = 12.9 Hz, 1 H), 2.44 (d, $J$ = 12.9 Hz, 1 H), 2.43 (b s, 1 H), 2.15 (d, $J$ = 15.3 Hz, 1 H), 1.72 (d, $J$ = 15.3 Hz, 1 H), 1.58 (m, 3 H), 1.37 (m, 4 H), 1.20 (m, 1 H).

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**Registry No.** **3**, 17530-61-9; **3** Pt(Cl)(acac) complex, 92473-64-8; **4**, 86508-21-6; **5**, 86508-19-2; **6**, 92542-51-3; **7**, 6671-66-5; **8**, 86508-22-7; **9**, 86508-23-8; **14**, 86508-24-9; **15**, 86508-25-0; **16**, 92473-65-9; **17**, 92473-63-7; **18**, 92473-66-0; $Pt(Cl)(acac)((CH_3)_2C{=}CHCH_3)$, 52451-10-2; $Pt(Cl)_2(Py)(C_2H_4)$, 12078-66-9; $Pt(Cl)(acac)(C_2H_4)$, 31781-77-8; $Pd(Cl)_2(PhCN)_2$, 14220-64-5; $Pd(Me)_2(PPh_3)_2$, 36485-69-5; $Pd(CD_3)_2(PPh_3)_2$, 86508-20-5; *cis*-$Pd(PPh_3)_2(Me)(I)$, 35655-02-8; $Pd(\eta^5\text{-}(C_5H_5)(\eta^3\text{-}C_3H_5)$, 1271-03-0; $Pt(PPh_3)_2(C_2H_4)$, 12120-15-9; Pt(Cl)(acac)(*trans*-$CH_3CH{=}CHCH_3$), 31941-76-1; $Pd(OAc)_2$, 3375-31-3; $Pd(PPh_3)_2(C_2H_4)$, 33395-22-1; 2-methyl-2-butene, 513-35-9.

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# Electrochemistry of Transition-Metal π-Complexes. 8.[1] Oxidation of Chromium, Molybdenum, and Tungsten Sulfur Ylide Complexes

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Electrochemical oxidation of $\lambda^6$-thiabenzene 1-oxide complexes 1–3[2] and $\lambda^4$-thiabenzene complexes 4–6[2] at a Pt electrode in methylene chloride is found to proceed in a chemically reversible manner if Cr is the central metal and partly or completely irreversibly for Mo and W as the central metals. Cyclic voltammetry and chronopotentiometry confirm a single electron oxidation in all cases. Chemical oxidation of the Cr derivative **1d** using $N(p\text{-}BrC_6H_4)_3PF_6$ as the oxidant precipitates the salt [**1d**]$PF_6$, which was characterized by analysis, spectroscopy, and magnetic moment. The redox potentials observed are discussed with reference to those found for the related complexes $M(arene)(CO)_3$ and $MCp(CO)_3^-$.

According to the molecular structure determined by single-crystal X-ray diffraction[3] the $M(CO)_3$ unit in $\lambda^6$-thiabenzene 1-oxide and in $\lambda^4$-thiabenzene complexes is bound solely to the dienyl part of the ylidic $(\eta^5\text{-}C_5R_5)S(O)R'$ or the $(\eta^5\text{-}C_5R_5)SR'$ ligand, formally charged negatively. Thus with respect to their chemical and redox properties one may expect these complexes to occupy a position intermediate between the neutral arene tricarbonyl complexes 7 and the cyclopentadienyl tricarbonyl anions 8 of the group 6 metals. A basic metal center is evidenced by, e.g., the facile nitrosylation of 1–3 leading to the corresponding $[ML(CO)_2NO]^+$ cations.[4,5] Protonation occurs at the 2-position of the ylidic ring ligand and yields cations $[M(diene)(CO)_3(solv)]^+$.[6] Reductive dealkylation with $LiBEt_3H$ transforms 1–3 into the anions $[M(C_5R_5SO)(CO)_3]^-$,[7,8] which react analogous to the cyclopentadienyl tricarbonyl anions with NO to give nitrosyl complexes $M(C_5H_3R_2SO)(CO)_2NO$[9] or with halogens to produce halo complexes $M(C_5H_3R_2SO)(CO)_3X$, X = Cl, Br, and I.[8]

Apart from these reactions where the redox step is coupled to changes in the ligand sphere, electrochemically effected electron transfer in an inert solvent and in the absence of potential ligands was thought to provide data for the comparison of the novel sulfur ylide complexes with the more common analogues 7 and 8. We present results on the electrochemical oxidation of sulfur ylide/complexes

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