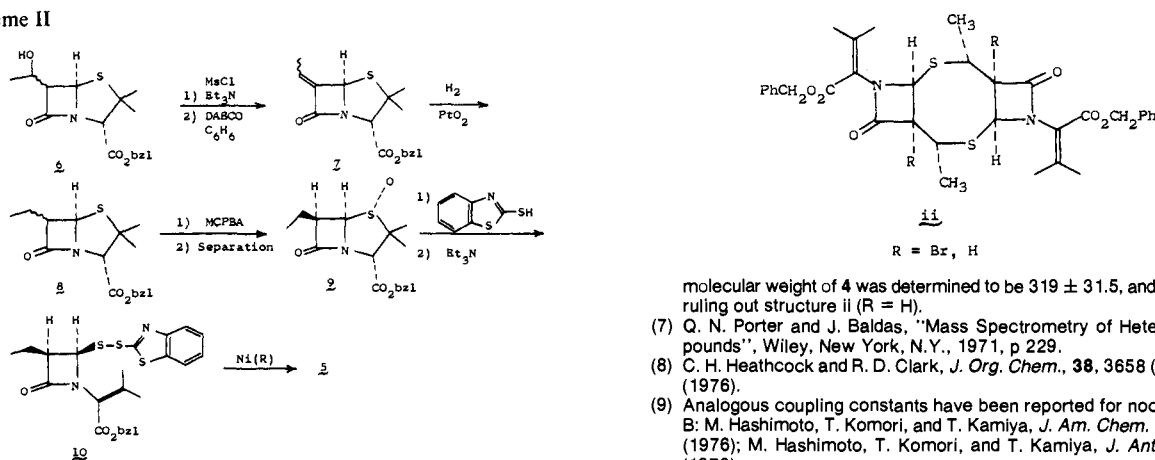


Scheme II



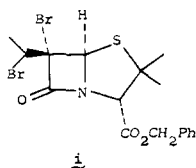
these values were obtained when the spectrum was recorded in $\text{Me}_2\text{CO}-d_6$: δ 3.15 (m, H_A), 3.21 (dd, $J_{AC} = 2.5$ Hz and $J_{BC} = 5$ Hz, H_C),⁹ and 3.55 (t, $J_{AB} = J_{BC} = 5$ Hz, H_B).

Degradation product **5** was independently synthesized in an unequivocal manner as depicted in Scheme II. A mixture of *cis*- and *trans*-(*R*)-hydroxyethylpenicillanates **6**⁴ was quantitatively converted to the corresponding mesylates¹⁰ using the procedure of Crossland and Servis,¹¹ and subsequently eliminated (1,4-diazabicyclo[2.2.2]octane, C_6H_6 , 80 °C, 77%) to a mixture of enelactams.¹⁰ Catalytic hydrogenation (PtO_2 , EtOAc) of **7** provided a mixture of 6-ethylpenicillanates **8** (90%)^{10,12} in which the expected *cis* isomer comprised 90% of the mixture. Sulfoxidation (MCPBA, CH_2Cl_2 , 25 °C) of **8** afforded a mixture of penams (92%) from which the major, crystalline (mp 77–79 °C) α -sulfoxide **9** (80%)^{10,13} was readily separated. Cleavage of the thiazolidine ring of **9** according to the method of Kamiya and co-workers¹⁵ followed by isomerization of the β,γ double bond into conjugation (Et_3N , CH_2Cl_2 , 25 °C) yielded the disulfide azetidinone **10** (85%).¹⁰ Finally, desulfurization of **10** ($\text{Ni}(\text{R})$, EtOH , 60 °C) produced azetidinone **5**, which possessed physical and spectral properties identical with those of the material obtained from the degradation of **2**.

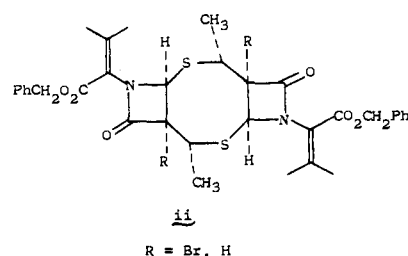
Acknowledgment. We thank Mr. J. Smith for mass spectral measurements, Mr. H. Flynn for recording the 300-MHz NMR spectra and performing the NOE experiments, and Dr. J. A. McCauley for the vapor phase osmometric molecular weight determinations.

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- molecular weight of **4** was determined to be 319 ± 31.5 , and thereby further ruling out structure **ii** ($\text{R} = \text{H}$).
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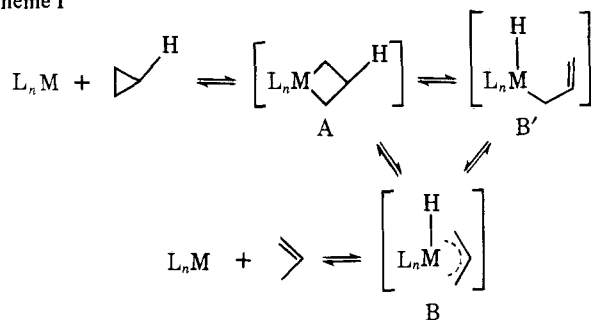
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Reactions of Platinum Metal Complexes with Strained-Ring Compounds: $\text{IrCl}(\eta^3\text{-C}_3\text{H}_4\text{C}_6\text{H}_5)[\text{P}(\text{C}_6\text{H}_5)_3]_2$, an Isolable η^3 -Allyl Metal Hydride Complex

Sir:

Transition-metal catalyzed rearrangements of strained-ring systems have received much attention in recent years.¹ One of the most widely studied reactions has been the ring opening of a cyclopropyl fragment to yield an isomeric olefin.²⁻⁴ An η^3 -allyl metal hydride intermediate (**B** in Scheme I) is often invoked in the mechanism, as it accounts for the variety and distribution of the olefinic products found, but it has never been directly observed in these reactions. In other important metal-catalyzed olefinic transformations (e.g., olefin metathesis,⁵ isomerization,⁶ and oligomerization⁷) the existence of an allyl metal hydride intermediate is strongly, but indirectly, suggested. We know of only three brief reports concerning the characterization of allyl metal hydride complexes.⁸⁻¹⁰ The compounds $\text{NiH}(\eta^3\text{-C}_3\text{H}_5)(\text{PPh}_3)$ and $\text{NiH}(\eta^3\text{-C}_3\text{H}_5)(\text{PF}_3)$,⁸ prepared at low temperatures, were found to decompose irreversibly above -30 °C. Between -40 and -50 °C, the PF_3 complex was shown to be in dynamic equilibrium with the corresponding nickel(0)- η^2 -propene complex. Byrne et al.⁹ have reported the ¹H NMR characterization of $\text{MoH}(\eta^3\text{-C}_3\text{H}_5)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$ and have shown that this complex exhibits similar dynamic behavior. In an attempt to prepare an iridium metalocyclobutane, i.e., **A** in Scheme I, we have isolated an η^3 -allyl metal hydride complex of formula $\text{IrCl}(\eta^3\text{-C}_3\text{H}_4\text{Ph})(\text{PPh}_3)_2$. This complex is very stable and does not exhibit dynamic behavior at ambient temperatures. We believe that this represents the first example of a stable, fully characterized, η^3 -allyl metal hydride complex.

Scheme I



As such it provides direct evidence for the viability of Scheme I in cyclopropane-to-olefin isomerizations and should serve as an excellent analogue for the rhodium(III) species often proposed in the catalytic processes cited above. Here we describe our initial work with this complex, including an x-ray structural determination.

When a suspension of $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$ ¹¹ in neat, degassed phenylcyclopropane is stirred under N_2 at 25 °C, the yellow solid dissolves slowly to yield a homogeneous orange solution from which an off-white solid is deposited. Upon recrystallization an analytically pure sample of $\text{IrClH}[\eta^3\text{-C}_3\text{H}_4(1\text{-Ph})](\text{PPh}_3)_2$, I, is obtained (unoptimized yield, 40%). Compound I exhibits a very strong, sharp IR absorption at 2208 cm^{-1} , which is characteristic of $\nu_{\text{Ir-H}}$, and an $\nu_{\text{Ir-Cl}}$ stretching frequency of 245 cm^{-1} . The low energy of this stretching frequency is indicative of a chloride atom occupying a position trans to a hydride atom in an octahedral complex of iridium(III).¹² The assignment of the 1 position of the phenyl ring is based on ¹H and ³¹P NMR spectroscopy.¹³

To obtain metrical details we carried out an x-ray diffraction study of I. The compound crystallizes in the orthorhombic space group $C_{2v}^9\text{-Pn}2_1a$ with four molecules in a cell of dimensions, $a = 14.902(2)$, $b = 11.016(2)$, and $c = 22.456(4)$ Å. A total of 3738 unique, significant [$F_0^2 > 3\sigma(F_0^2)$] data were collected in a fashion normally used in this laboratory.¹⁴ A Patterson synthesis revealed the structure, which has been refined conventionally to a current residual R index on F_0 of 0.029. Atomic parameters obtained at the current stage of refinement are available as supplementary material (see paragraph at the end of the paper). A representation of the inner coordination sphere of the molecule is shown in Figure 1, which also contains the atom identification scheme used. The complex, in which the allyl group occupies two coordination sites, adopts a pseudo-octahedral geometry: P(1)–Ir–P(2), 101.57(6); P(1)–Ir–Cl, 86.72(6); P(2)–Ir–Cl, 103.83(6); Cl–Ir–H, 171(2); P(1)–Ir–H, 87(2); P(2)–Ir–H, 83(2)°. Note the extremely long Ir–Cl bond which presumably results from the trans influence of the hydride ligand. This value, 2.549(2) Å, may be compared with that observed for a related iridium(III) η^3 -allyl complex $[\text{IrCl}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})(\text{PPh}_3)_2][\text{PF}_6]$,¹⁵ 2.389(3) Å.

The geometry of the η^3 -allyl group is normal¹⁶ as are the Ir–C(allyl) distances. Possible differences between the Ir–C(1) vs. Ir–C(3) and the C(2)–C(3) vs. C(1)–C(2) distances may result from the phenyl substitution at atom C(3). However, there is no demanding evidence for substantial conjugation between the phenyl and allyl groups; little overlap should be expected as the dihedral angle between these groups is 51°.

The orientation of the allyl group is noteworthy. Atom C(2) is closer to the hydride ligand than to the chlorine atom, the C(2)–H distance being 2.42(7) Å. This orientation may be responsible for the observed stability of I with respect to reductive coupling of the allyl and hydride ligands. For I to undergo hydride migration from the metal to a terminal carbon atom, as deduced by Byrne et al.⁹ for $\text{MoH}(\eta^3\text{-C}_3\text{H}_5)$ -

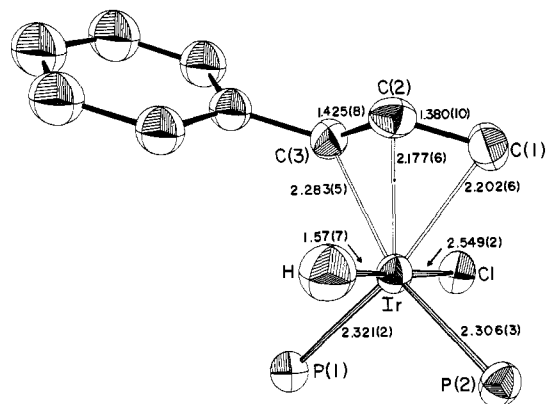


Figure 1. A perspective view of the inner coordination sphere of $\text{IrClH}[\eta^3\text{-C}_3\text{H}_4(1\text{-Ph})](\text{PPh}_3)_2$. The vibrational ellipsoids are drawn at the 50% probability level. The labeling scheme is also shown.

$(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$, the allyl group would need to rotate 180°. This rotation may be unfavorable, as repulsive interactions between the allyl and phosphine phenyl groups could result. In fact, the structural results suggest that the preferred decomposition pathway for I might be hydride migration to atom C(2), resulting in formation of an iridium-metalcyclobutane.

Since η^3 -allyl metal hydride complexes are implicated in the cyclopropane-to-olefin transformation, we felt that I might also possess catalytic properties despite its stability. However, upon treating a mixture of phenylcyclopropane and I (1000:1 mol ratio) in a manner similar to that employed by Roth and co-workers,¹⁷ we were unable to detect any olefin. Yet we have observed that a substantial quantity of α -methylstyrene is produced in the initial reaction of $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$ with phenylcyclopropane. Its production, as the reductive elimination product from the 2-phenyl allyl isomer of I, is in accord with earlier reports of phenylcyclopropane ring opening by rhodium(I)¹⁸ or platinum(II)¹⁹ complexes. The mechanism by which this olefin is produced is under investigation.

Further evidence for the thermodynamic stability of I comes from the observation that the reaction of allylbenzene with $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$ produces I in $\approx 80\%$ yield. Presumably this takes place by initial olefin complexation followed by insertion into the allylic C–H bond. This reaction is thus the reverse of the decomposition pathway observed for $\text{NiH}(\eta^3\text{-C}_3\text{H}_5)(\text{PF}_3)$ and $\text{MoH}(\eta^3\text{-C}_3\text{H}_5)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$, as mentioned above. Allylic C–H bond activation of this type is often the suggested initiation step for the catalytic olefin transformations, in which allyl metal hydride complexes have been implicated.^{5–7}

The details of the reactions cited above are currently being explored and promise to yield information pertinent to transition-metal-promoted C–C and C–H bond activations²⁰ as well as olefin transformation catalysis.

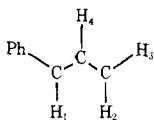
Acknowledgments. We thank Matthey-Bishop, Inc., for the generous loan of precious metals used in our studies. T.H.T. thanks Northwestern University for the support of a Doctoral Year Fellowship. This work was supported by the National Science Foundation.

Supplementary Material Available: Tables of atomic parameters (4 pages). Ordering information is given on any current masthead.

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ppm, ν_B 0.87 ppm, downfield with respect to external 85% H_3PO_4 ($^2J_{\text{P}(1)-\text{P}(2)} = 5.0$ Hz)).

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Approaches to Homogeneous Reduction of Carbon Monoxide: Reaction of Niobium Hydrides with Coordinated CO

Sir:

There is currently intense interest in homogeneous catalysis of reactions of carbon monoxide and hydrogen ("synthesis gas"), with much of the recent activity focusing on metal clusters as potential catalysts.^{1,2} Mechanistic considerations applied to possible pathways involving *mononuclear* catalytic sites suggest that formation of the first C-H bond may be a key step. An alternative to insertion of CO into a metal-hydrogen bond, which does not appear to be a feasible transformation,³ would be nucleophilic attack by a hydride on a coordinated carbonyl. Such reactions have been found to lead to formyl,³ hydroxymethyl,⁴ and methyl^{5,6} complexes, using boron hydride reagents. A *catalytic* process involving such a step would require a transition metal hydride capable of exhibiting hydridic character, which has been observed only for several complexes of titanium⁷ and zirconium.^{8,9} Examples of the reduction of CO to methane¹⁰ or to alcohols^{11,12} employing these metals have recently been reported. However, these hydrides react readily with water and alcohols, the reaction products, as well, apparently precluding their use in catalytic systems.

We have chosen to direct our attention to the next group of the periodic table, in hopes that hydride complexes would be stable to the reaction products while still maintaining some hydridic character. The complexes Cp_2NbH_3 and $\text{Cp}_2\text{NbH}(\text{CO})$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) were found to be stable to water and ethanol at room temperature but to slowly reduce

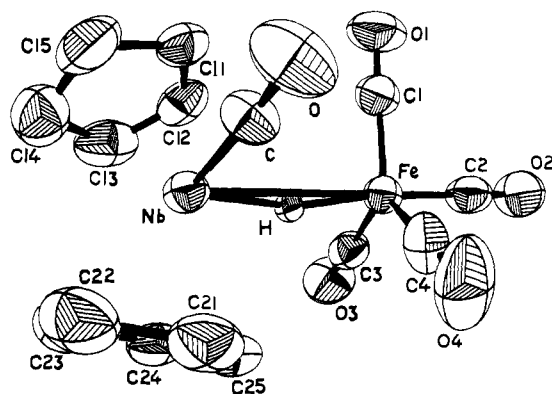


Figure 1. Molecular structure of $(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})\text{Nb}(\mu\text{-H})\text{Fe}(\text{CO})_4$ (Cp ring hydrogens are not shown).

acetone,¹³ suggesting that they might possess the necessary reactivity. $\text{Cp}_2\text{NbH}(\text{CO})$ reacts slowly ($T_{1/2} \approx 1$ day) at 140 $^\circ\text{C}$ under H_2 to give an insoluble brown solid.¹⁴ No new products can be detected in solution, but analysis of the gas phase¹⁵ shows the presence of methane and ethane, each formed in ~ 2 -5% yield (based on Nb complex consumed), plus trace amounts of propane. The origin of these products is established by labeling studies: use of D_2 instead of H_2 gives a roughly equal mixture of CD_4 and CHD_3 , while reduction of $\text{Cp}_2\text{NbH}(\text{CO})$ gives $^{13}\text{CH}_4$, demonstrating that methane is produced by CO reduction. In contrast, however, the higher alkanes show no incorporation of either label, and hence are formed by a different process, most probably degradation of the Cp rings.¹⁶ Use of an H_2 -CO gas mixture results in no significant change in methane yield (although the ethane yield decreases, consistent with the conclusion that these are produced by different pathways).

The vigorous conditions required to bring about attack on CO by the niobium hydride can be ascribed, at least in part, to the low hydridic character (in comparison with group 4 hydrides). Another possible factor, however, is the character of the CO: for attack by hydride the CO should be as electrophilic as possible, but the low stretching frequency of $\text{Cp}_2\text{NbH}(\text{CO})$ ($\nu_{\text{CO}} 1900 \text{ cm}^{-1}$) suggests, on the contrary, that the CO is relatively electron rich. In contrast, $\text{Fe}(\text{CO})_5$ (which should be more readily attacked by a hydridic reagent³) reacts rapidly with Cp_2NbH_3 , even at room temperature. Evidence that hydride attack on CO takes place was obtained by monitoring the ^1H NMR during the reaction;¹⁷ in addition to starting material and product peaks, a new singlet at δ 14.3 appears and grows to a maximum at early stages before disappearing as the reaction goes to completion. The shift of this signal is characteristic of metal formyl complexes³ and strongly suggests that an intermediate closely resembling $(\text{HCO})\text{-Fe}(\text{CO})_4^-$ (probably strongly ion paired or even bonded through the acyl oxygen to the niobium) is involved in the reaction pathway.

Unfortunately, although the use of this mixed-metal system does appear to facilitate the attack of hydride on CO, it does not lead to reduced CO: the overall products are H_2 (1 mol per Nb) and a new compound, characterized by elemental analysis, IR and NMR spectroscopy, and x-ray crystallography¹⁸ as $\text{Cp}_2(\text{CO})\text{Nb}(\mu\text{-H})\text{Fe}(\text{CO})_4$ (Figure 1). This compound may be viewed as an adduct between $\text{Cp}_2\text{NbH}(\text{CO})$ and the unsaturated fragment $\text{Fe}(\text{CO})_4$, with donation through a bridging hydrogen as well as the metal-metal bond.¹⁹ Even though neither of the systems examined leads to catalytic CO reduction, the postulated correlation between CO-reducing ability and the nucleophilic and electrophilic character of the metal hydride and metal carbonyl, respectively, seems to be valid, suggesting promising directions for future work in this area.