A 1-Norbornene Adduct of a Transition Metal and an Electrochemical Study of the Bridgehead Olefin Complex

Gavin D. Jones and David A. Vicic*

Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701

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Summary: Treatment of a slurry of $(PCy_3)_2NiCl_2$ *in pentane with 1-norbornyllithium did not lead to the expected bis(1-norbornyl) nickel complex but instead led to formation of a 1-norbornene adduct, which has been structurally characterized. The X-ray data and the electrochemistry of the 1-norbornene complex suggest a metallacyclopropane extreme of olefin binding, stemming from the highly reactive nature of the bridgehead double bond.*

Double bonds located at a bridgehead position of fused-ring systems have fascinated chemists for many years.[1−3] The distortion of the π bond in these molecules caused by twisting often imparts reactivity atypical of a normal C−C double bond.[3] The appearance of bridgehead double bonds in important natural products such as taxol[4−6] has also sparked a great deal of interest in learning about the susceptibility of these olefins to a variety of reaction conditions that might be employed in a total synthesis. Additionally, there is much impetus for developing methods to systematically study the reaction chemistry of the bridgehead double-bond functionality, as the removal of a bridgehead double bond in the calicheamicin/esperamicin family of enediyne toxins is believed to be a primary step in the activation process leading to arene-1,4-diyl formation, H-atom abstraction, and DNA cleavage.[7−10]

While bridgehead double bonds in larger ring systems are known to be relatively stable, the existence of smaller ring systems with bridgehead double bonds such as 1-norbornene (**1**) has been harder to evaluate, as Wiseman predicted that the strain in bridgehead alkenes is closely related to the strain of the corresponding *trans*-cycloalkene.[11] Indirect evidence of the anti-Bredt[12] olefin **1** has been obtained by trapping transiently generated **1** with a variety of organic reagents or by monitoring the thermal rearrangement products of precursor derivatives.[13−17] A number of computational methods have also been applied to **1** in order to better understand the structure, energetics, and reactivity of this highly sensitive molecule.[18−23] However, as no direct observation of **1** in solution has ever been reported and no reversible trapping agent for this molecule has ever been prepared, its chemistry has been difficult to study.

A transition-metal binding approach, similar to what has been employed in benzyne chemistry,[24−29] could be one possible strategy to obtain stable precursors of these short-lived compounds for synthetic and mechanistic studies. While transition-metal complexes of larger bridgehead double bonds are known[30−35] or speculated

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* To whom correspondence should be addressed. E-mail: dvicic@uark.edu.

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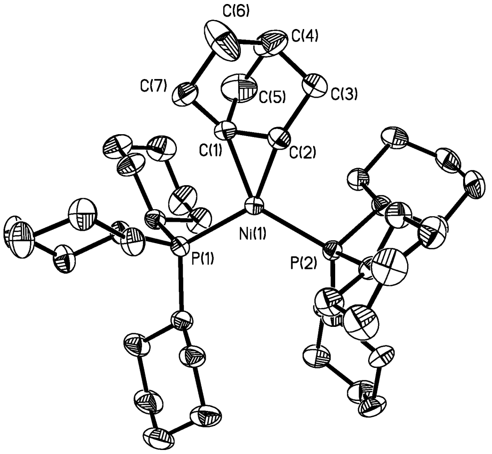
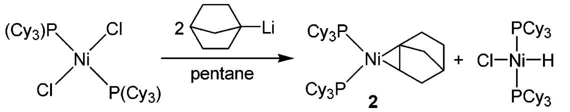


Figure 1. ORTEP diagram of the 1-norbornene adduct **2**. Ellipsoids are shown at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ni(1)−C(1) = 1.949(4), Ni(1)−C(2) = 1.957(5), C(1)−C(2) = 1.454(6), Ni(1)−P(1) = 2.186(3), Ni(1)−P(2) = 2.1878(16).

to have formed in metal-mediated reactions,[36−38] the trapping of smaller, more reactive bridgehead double bonds remains much more problematic, especially since trapping must usually be competitive with dimer formation resulting from formal 2 + 2 cycloaddition reactions. Here we report a new method to prepare a transition-metal adduct of 1-norbornene that overcomes the problems associated with competitive trapping and also describe the unexpected electrochemistry of this new transition-metal adduct.

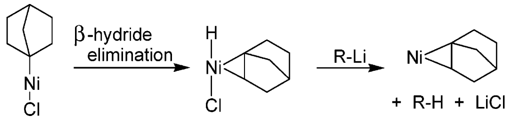
Treatment of a slurry of $(PCy_3)_2NiCl_2$ in pentane with 2 equiv of 1-norbornyllithium was found to afford $(PCy_3)_2NiHCl$[39] and a new product (**2**; eq 1) that displayed two doublets in the $^{31}P\{^1H\}$ NMR spectrum.



(1)

The ratio of $(PCy_3)_2NiHCl$ to **2** was 1:22 after 10 min. Since the $^{31}P\{^1H\}$ NMR data for **2** could also be consistent with a *cis*-$(PCy_3)_2Ni$(norbornyl)Cl complex, crystals of **2** were grown to determine the true identity of the new compound. X-ray analysis clearly identifies the new product as an η^2-bound adduct of 1-norbornene, and the ORTEP diagram is shown in Figure 1.

The reaction conditions appear to be key in the overall transformation to the η^2-bound adduct.[40] The starting material $(PCy_3)_2NiCl_2$ is highly insoluble in pentane; thus, it can be expected that any alkylated nickel complex formed in situ is then exposed to a large excess of norbornyllithium. These basic conditions may be critical in removing HCl that could possibly result from a β-hydride elimination reaction, as described in eq 2.

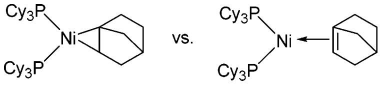


(2)

An alternative mechanism may involve formation of a Ni(norbornyl)$_2$ species, which then eliminates hydrocarbon en route to **2**. One equivalent of norbornane relative to nickel starting material is produced in the reaction described in eq 2. Repeating the lithiation in a 3:1 mixture of pentane and furan did not lead to any furan adducts of norbornene,[15] consistent with an intramolecular process in which olefin **1** is never released from the metal.

Of note, the C(1)−C(2) bond length of 1.454(6) Å is especially long for a carbon−carbon double bond. $(PCy_3)_2Ni(\eta^2(C,C)$-methyl methacrylate) (**3**) is the only other olefin complex containing the $(PCy_3)_2Ni$ fragment that has been crystallographically characterized. Even with the presence of an electron-withdrawing ester group, the coordinated double bond in **3** (1.410(13) Å)[41] was found to be shorter than that observed in **2**. DFT calculations predict a C═C bond length of 1.3584 Å for uncomplexed **1**.[23]

Chart 1



A **B**

The crystallographic data thus support the metallacyclopropane extreme of olefin coordination for compound **2** (**A**; Chart 1) instead of the Dewar−Chatt description, which does not affect the oxidation state of the metal (**B**; Chart 1).[42] To determine if the bonding is more a result of a strongly π-basic metal or of the unusual nature of the bridgehead double bond of 1-norbornene, electrochemical measurements were performed on a series of related olefin adducts of $(PCy_3)_2Ni$ (Table 1). Both $(PCy_3)_2Ni(\eta^2$-1-hexene) and $(PCy_3)_2Ni(\eta^2$-ethylene) display three sequential oxidations in the cyclic voltammograms, consistent with stepwise oxidation of a Ni(0) species to Ni(III). Compound **2**, on the other hand, displays only one irreversible oxidation. One possible interpretation of these data is that the irreversible oxidation of **2** is in fact an oxidation of Ni(II) to Ni(III), consistent with the metallacyclopropane character

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(40) **Preparation of $(PCy_3)_2Ni(\eta^2$-1-norbornene) (2)**: 1-norbornyllithium (15.3 mL, 0.11 M in pentane) was added to a slurry of $(PCy_3)_2NiCl_2$ (581 mg, 0.84 mmol) and pentane (100 mL) and stirred for 10 min. The resulting solution was passed over a 1 cm pad of alumina, and thorough rinsing with pentane yielded an orange filtrate. The solvents were evaporated, and the crude product was further purified by extraction with pentane and additional filtration over a 1 cm pad of alumina. Removal of solvents yielded 398 mg (66%) of an orange solid. Crystals were grown from a concentrated solution of **2** in pentane at −30 °C. $^{31}P\{^1H\}$ NMR (C_6D_6, 30 °C, 121.5 MHz): δ 44.14 (d, J = 20.7 Hz), 39.63 (d, J = 20.8 Hz). Anal. Calcd (found) for $C_{43}H_{76}NiP_2$: C, 72.36 (72.12); H, 10.73 (10.49).

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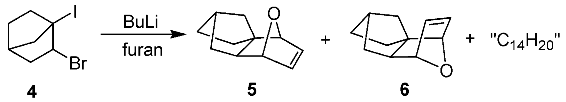
Table 1. Electrochemical and NMR Data for Olefin Adducts of $(PCy_3)_2Ni$ and Related Compounds[a]

compd	oxidn potential (V)	$^{31}P\{^1H\}$ NMR chem shift (ppm)
2	−0.23 only	44.1, 39.6 (C_6D_6)
$(PCy_3)_2Ni(\eta^2\text{-1-hexene})$	−0.59, 0.16, 0.98	35.0 (C_6D_{12})[43]
$(PCy_3)_2Ni(\eta^2\text{-ethylene})$	−0.45, 0.36, 1.04	34.4 (C_6D_6)
$(dippe)Ni(CH_3)_2$[44]	−0.02 only	77.0 (C_6D_6)

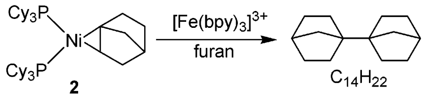
[a] All potentials were measured in THF solution using 0.1 M Bu_4NPF_6 and 3 mM Ni complex and referenced vs Ag/Ag^+. Scan rate: 10 mV/s. Values are reported as anodic peak potentials.

of the organometallic fragment. The energy of the oxidation is not unreasonable for a Ni(II)−dialkyl species, and the oxidation of a related compound, (dippe)-$Ni(CH_3)_2$ (dippe = 1,2-bis(diisopropylphosphino)ethane), was found to occur irreversibly at −0.02 V. A *cis*-dialkyl complex containing alkyl groups more donating than methyls should therefore occur at more reducing potentials, such as that observed for **2**. The $^{31}P\{^1H\}$ NMR chemical shifts of **2** also appear much more downfield than for reported Ni(0) complexes (Table 1), which may lend additional support for Ni(II) character in **2**. Assuming then a Ni(II) oxidation state for **2**, we conclude that relief of ring strain in the unusual bridgehead double bond is the primary reason for both the elongated C−C bond lengths and the anomalous metal oxidation state.

The preliminary reactivity of **2** was also explored. We wondered whether oxidation could be used as a trigger to release reactive **1** in solution. If so, oxidation could be a facile way to explore the scope of additions of small molecules to **1**. Keese and co-workers reported that chemically generated **1** in the presence of furan led to the formation of furan adducts and norbornene dimers (eq 3).[15] We found, however, that oxidation of **2** by Fe(III) produced dinorbornyl as the only identifiable organic compound (eq 4). Further studies directed at olefin release and functionalization are underway.



(3)



(4)

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Supporting Information Available: Text giving general methods and CIF files giving X-ray data for compound **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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