to generate an η^4-arene intermediate which results from the retention of aromaticity in the noncoordinated rings. Our results indicate that similar effects reverse the direction of the exchange reaction if the η^4-arene complex is the starting material rather than an intermediate, that the η^4-benzene in $[Cr(\eta^4\text{-}C_6H_6)(CO)_3]^{2-}$ is an exceptionally labile arene ligand, and that reductive activation arene exchange reactions can lead to products which cannot be prepared pure by other routes.

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Registry No. 1, 12082-08-5; 2^{2-}, 115677-75-3; 4, 12110-37-1; 5^{2-}, 57220-00-5; 6^-, 87136-08-1; $[NEt_4]$6, 87145-02-6; 7a, 105063-49-8; 7b, 105063-45-4; 8a, 12111-62-5; $K[C_{10}H_8]$, 4216-48-2; $Na[C_{10}H_8]$, 3481-12-7; $K[1,4\text{-}C_{10}H_6Me_2]$, 60183-86-0; $Na[1,4\text{-}C_{10}H_6Me_2]$, 60183-89-3; $Na[1\text{-}C_{10}H_7Me]$, 3620-00-6; $K[1\text{-}C_{10}H_7Me]$, 115677-76-4.

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Nucleophilic Cleavage of the sp^3 Carbon–Oxygen Bond in Alkoxycarbene Complexes: Conversion of 2-Oxacyclopentylidene Ligands to Pyridinium-Substituted Acyl Ligands

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Summary: The cationic carbene complexes $Ir(CR{=}CRCR{=}CR)({=}CCH_2CH_2CHR'O)(PPh_3)_2(CO)^+BF_4^-$ [R = CO_2CH_3; R′ = H, **1**; R′ = CH_3, **5**] react with pyridine to form the acyl complexes $Ir(CR{=}CRCR{=}CR)(COCH_2CH_2CHR'NC_5H_5)(PPh_3)_2(CO)^+BF_4^-$ [R′ = H, **3**; R′ = CH_3, **6**]. The solid-state structure of the novel pyridinium-substituted acyl complex **3** has been determined by X-ray crystallography.

The role of metal carbene complexes in olefin metathesis,[1] in certain olefin polymerizations,[2] and as synthetic intermediates[3] has generated extensive interest in the properties and reactivity of this prominent compound class. In the area of organic synthesis, 2-oxacycloalkylidene complexes are attractive due to ease of ligand formation,[4] modification,[5] and subsequent removal of the metal.[6] With respect to carbene modification, the isolobal analogy of alkoxycarbene complexes and esters has been a useful guide for development of carbene reactions.[7,8a] It is now widely recognized that alkoxycarbene complexes exhibit four primary reactivity patterns (Figure 1):[8b] ligand substitution (1), nucleophilic attack at the carbene carbon (2), often resulting in heteroatom exchange (2′), deprotonation at the α-carbon (3), and addition of unsaturated species across the metal–carbon double bond (4). A less commonly observed fifth mode of reactivity is nucleophilic attack at the sp^3 carbon–oxygen bond (5).[9–11]

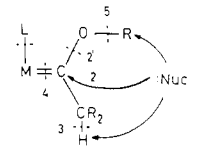

Figure 1.

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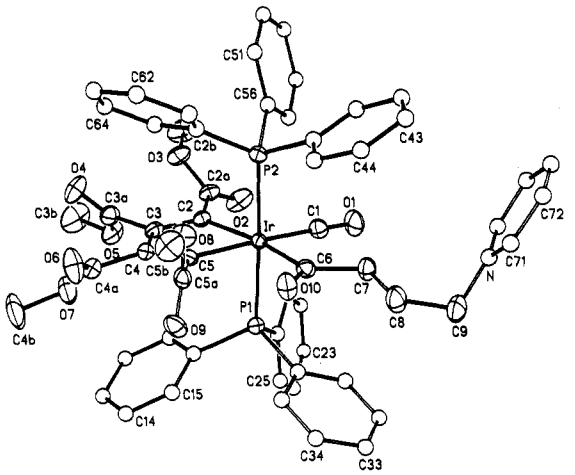
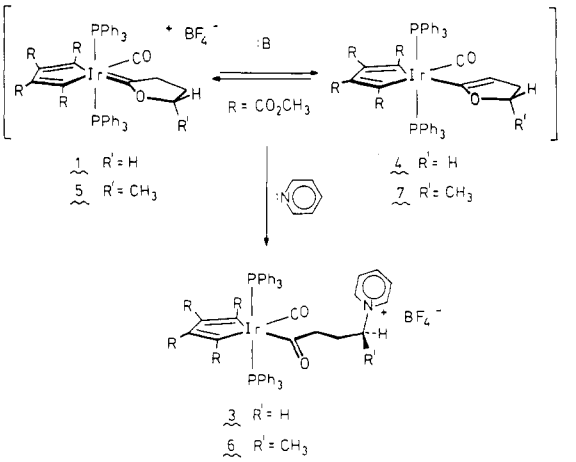


Figure 2. Molecular structure and labeling scheme for **3** ($-BF_4^-$ counterion). Bond distances (Å): Ir–C(2), 2.161 (4); Ir–C(5), 2.102 (4); Ir–C(6), 2.136 (4). Bond angles (deg): P(1)–Ir–C(1), 90.6 (2); P(1)–Ir–C(2), 90.3 (1); P(1)–Ir–C(5), 87.3 (1); P(1)–Ir–C(6), 89.1 (2); P(2)–Ir–C(1), 91.4 (2); P(2)–Ir–C(2), 88.4 (1); P(2)–Ir–C(5), 90.7 (1); P(2)–Ir–C(6), 91.8 (2); C(1)–Ir–C(2), 102.5 (2); C(1)–Ir–C(6), 89.3 (2); C(2)–Ir–C(5), 77.3 (2); C(5)–Ir–C(6), 90.9 (2).

We report herein the pyridine-induced cleavage of substituted sp^3 carbon–oxygen bonds in electrophilic carbene complexes. In the case of bond cleavage at a secondary carbon center, the mild conditions of this reaction are remarkable on the basis of established reactivity trends for other electrophilic carbenes as well as organic esters and lactones.[12]

We recently reported the synthesis of the first metallacycle–carbene complex **1** by treatment of the cationic metallacycle $\overline{Ir(CR{=}CRCR{=}CR)}(PPh_3)_2(CO)(NCCH_3)^+$-$BF_4^-$ (**2**, R = CO_2CH_3) with 3-butyn-1-ol.[13] In the course of examining the reactivity of this compound, we have now discovered that addition of excess pyridine (aqueous) (200 μL, 2.5 mmol) to $CDCl_3$ solutions of **2** (150 mg, 0.13 mmol, 0.05 M) at 23 °C results in nearly quantitative conversion to the pyridinium–acyl complex **3**.[14] We were unable to confirm the presence of an acyl ligand in **3** by infrared spectroscopy as a single band in the acyl region is observed at 1625 cm^{-1}; the location of a pyridinium ion stretching mode.

Comparison of the structure for pyridinium acyl **3** (Figure 2)[15] to that for carbene precursor **1**[13] indicates relief



of steric strain in the conversion of **1** to **3**. The P(2)–Ir–C(2) and P(1)–Ir–C(2) angles are increased to 88.4° and 90.3°, respectively (from 85.0 and 88.4° in **1**), and the C(1)–Ir–C(6) and C(5)–Ir–C(6) angles are decreased to 89.3° and 90.9°, respectively (from 91.5° and 94.8° in **1**). The alkyl chain of the acyl ligand is extended so as to place the pyridine substituent at a maximum distance from the metal center.

When the reaction of **1** and pyridine is followed by ^1H NMR spectroscopy, we observe the transient formation of a third species, the originally expected vinyl ether complex **4**. We independently synthesized **4** in nearly quantitative yield from the reaction of **1** and PMe_3 in $CHCl_3$ solution at 23 °C. Treatment of isolated vinyl ether complex **4** (0.004 mmol, ~0.01 M) with $C_5H_5NH^+BF_4^-$ (0.04 mmol, ~0.10 M) in CD_3CN leads to rapid formation of carbene **1** which slowly (days) undergoes clean conversion to acyl complex **3**. Complex **1** is stable to PPh_3 under similar conditions. There is no evidence for competitive cleavage of the unhindered methyl ester substituents on the metallacycle ring during the **1** to **3** conversion.

The surprisingly facile and selective nature of this ring opening reaction led us to examine the effect of substitution at C-3 of the carbene ligand. Reaction of metallacycle **2** and 4-pentyn-2-ol generates the desired 3-methyl-2-oxacyclopentylidene complex (**5**) in 95% isolated yield.[14] At 23 °C an equilibrium is established between **5** (14.2 mg, 0.012 mmol, ~0.04 M) and **7** in the presence of excess pyridine (2 μL, 0.025 mmol) in $CDCl_3$ ($K_{eq} = 9.4 \times 10^{-3}$). Heating a chloroform solution of **5** (164 mg, 0.14 mmol, 0.01 M) and pyridine (aqueous) (1 mL, 12.4 mmol) at reflux leads to slow formation of the pyridinium-substituted acyl complex **6** in 63% yield.[14] In contrast, reaction of **5** and pyridine in C_6D_6 leads to immediate precipitation of $C_5H_5NH^+BF_4^-$ and quantitative formation of the neutral vinyl ether complex **7**.[14] Thus, choice of solvent as well as nucleophile dictates the reaction course.

It is clear that the electrophilic nature of the cationic

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(14) Complexes **3–7** have been characterized by ^1H NMR, ^{13}C NMR, IR, and mass spectroscopy and microanalysis. Details are provided as supplementary material.

(15) Crystal data for **3** (23 °C): $[C_{58}H_{53}IrNO_{10}P_2][BF_4]\cdot C_4H_8O$, triclinic; $P\bar{1}$; a = 12.157 (3), b = 12.133 (3), c = 23.080 (6) Å; α = 78.41 (2), β = 77.45 (2), γ = 61.87 (2)°; U = 2911 (2) Å^3; Z = 2; D_{calcd} = 1.525 g cm^{-3}; μ(Mo Kα) = 25.34 cm^{-1}. A Nicolet R3m/μ diffractometer was used to collect 9392 data (4° ≤ 2θ ≤ 48°) of which 9132 were independent ($R_{\mu\tau}$ = 1.68%) and 7912 with $F \geq 5\sigma(F_o)$ were observed. No correction for absorption was applied (T_{max}/T_{min} = 1.12). The structure was solved by Patterson methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located and isotropically refined except for those associated with the THF molecule of solvation (these were ignored). The phenyl rings were constrained to rigid, planar hexagons (C–C = 1.395 Å). At convergence; R = 3.04%, R_w = 4.04%, GOF = 1.009, Δ/σ = 0.042, $\Delta(\rho)$ = 0.74 e Å^{-3}, and N_o/N_v = 9.00. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

iridium center in 1 and 5 plays a major role in the chemistry reported here. The expected deprotonation at the α-carbon atom is competitive with ring opening, but reversible, thereby allowing eventual conversion to acyl products. We are currently examining the scope of this reaction in order to determine if, under the proper conditions, it will prove to be general for other mild nucleophiles and substituted electrophilic carbene ligands.

Acknowledgment. Partial support from the Academic Senate at the University of California, San Diego, is gratefully acknowledged.

Supplementary Material Available: Listings of fractional coordinates, bond distances, bond angles, hydrogen atom coordinates, and thermal parameters and analytical and spectroscopic characterization of all new compounds (10 pages); a table of structure factors (47 pages). Ordering information is given on any current masthead page.

Fundamental Processes at Polynuclear Centers. Kinetic Analysis of the Reaction of a Carbon–Nitrogen Double Bond with the $Rh_2(\mu\text{-}H)_2$ Core of Binuclear Rhodium Hydrides

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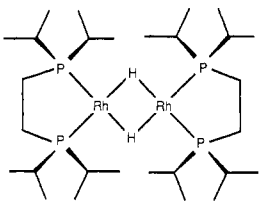
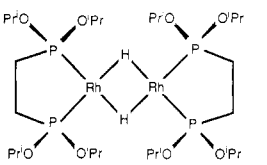
Summary: The binuclear rhodium hydrides $[(R_2PCH_2CH_2PR_2)Rh]_2(\mu\text{-}H)_2$ (R = Pr^i, **1a**; R = OPr^i, **1b**) react with *N*-benzylideneaniline to afford μ-amido hydride complexes in good yield. Spectroscopic monitoring of the reaction at low temperatures revealed that the reaction proceeds through an intermediate stable only below −50 °C; above this temperature, the intermediate decomposes to the amido hydride product. The two steps in this transformation were analyzed kinetically via $^{31}P\{^1H\}$ NMR spectroscopy. The structure of the intermediate is proposed to have a side-on bonded μ-imine ligand which collapses via migratory insertion of the carbon–nitrogen double bond into a terminal hydride bond.

The migratory insertion of unsaturated organic functionalities into metal–carbon and metal–hydride bonds is an important primary reaction in organotransition-metal chemistry. In addition to forming one of the fundamental reaction steps in various homogeneous catalytic hydrogenation[1] and oligomerization cycles,[2] many types of stoichiometric insertions have found wide application in organic synthesis.[3]

Generally, the mechanisms of the migratory insertion process are well understood in those reactions where only one metal center is involved.[4] However, in polynuclear systems, insertion reactions are less common and may be more complex mechanistically. This is not only due to the presence of reactive metal–metal bonds but also because the hydride or alkyl bond that is being formally "inserted into" may be in a bridging mode of ligation. As part of our continuing research in the area of the fundamental reactivity patterns in polynuclear systems,[5] we herein report the apparent "insertion" of an imine carbon–nitrogen double bond into the highly reactive four-center, four-electron $Rh_2(\mu\text{-}H_2)$ core of a family of binuclear rhodium hydrides incorporating chelating phosphine ligands.

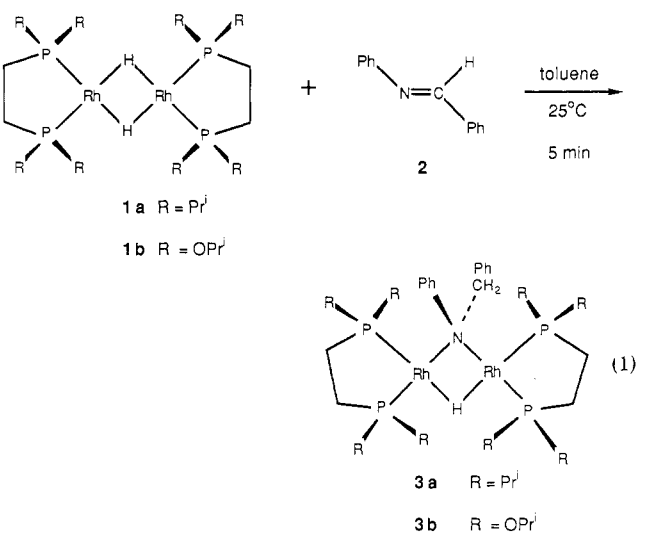


1a



1b

The binuclear rhodium hydrides $[(R_2PCH_2CH_2PR_2)Rh]_2(\mu\text{-}H)_2$ (R = Pr^i, **1a**; R = OPr^i, **1b**)[5a,b] react readily with 1 equiv of the *N*-benzylideneaniline, $(C_6H_5)N{=}CH(C_6H_5)$[6] (**2**), to afford the binuclear μ-amido–hydride complexes **3a** and **3b** in 80–85% isolated yields[7] (eq 1). Spectroscopic



(1)

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(3) In particular, insertions involving organozirconium compounds have been used extensively in organic synthesis. For a recent review, see: Negishi, E.; Takahashi, T. *Synthesis* **1988**, 1.

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(7) **Preparation of 3a.** To a stirred solution of **1a** (0.164 g, 0.22 mmol) in toluene (20 mL) was added 0.081 g of *N*-benzylideneaniline (**2**, 2 equiv). Within 5 min, a deep green to orange color change was complete, and the toluene was removed under vacuum. The orange residue was recrystallized from toluene/hexanes, yielding 0.167 g (82%) of orange crystals of **3a** after two recrystallizations. An identical procedure using **1b** was employed to yield **3b** in 84% yield.

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