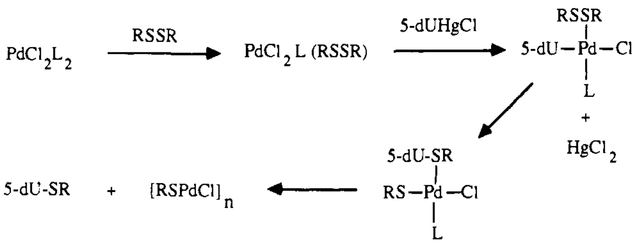
Scheme II



cystamine reaction provides useful entry to C-5 linker arms terminating by a primary amino group. An attempt to link a thiol group on the end of a five-atom chain by the reaction of 1,2-dithiane with 5-(chloromercurio)-2′-deoxyuridine and $Li_2PdCl_4$ in methanol gave essentially no coupled product. This result may be a function of competing reactions between disulfide and Pd(II). In the absence of 5-(chloromercurio)-2′-deoxyuridine there is a relatively rapid reaction between Pd(II) and organic disulfides, including 1,2-dithiane, to give unidentified yellow-orange complexes.

Preliminary studies with 5-chloromercuriocytidine show that it couples as well to disulfides. However, mercurated 2′-deoxyuridine 5′-monophosphate gave very little C-5 substituted product with *n*-butyl disulfide. The primary product following $H_2S$ workup was primarily 2′-deoxyuridine 5′-monophosphate.

Other synthetic sequences[21-23] have been described for generating thioether linkages at C-5 but none appear to offer the simplicity and apparent versatility of the current reaction.

The disulfide coupling reaction appears to represent an example of an unexplored area of organopalladium chemistry. Although it was recently established that aryl sulfides can be synthesized via either organonickel or organopalladium intermediates, these reactions proceed under quite different conditions (strongly basic and elevated temperatures) involving oxidative addition of transition-metal complexes to aryl halides and thiolate anions.[24-27]

Mechanistic studies up to this point have been rather limited, but it is possible to propose a rational mechanism on the basis of literature precedence and on the basis of a number of relatively simple observations and experiments. It was established at the outset that Pd(II) is an absolute requirement. No reaction occurs in its absence. Consequently there is no direct exchange reaction with the disulfide similar to that observed between halogens and arylmercury compounds (leading to aryl halides), nor is the coupling reaction observed when Pd(0) [as $Ph_3P)_4Pd$] is used in place of Pd(II). The disulfide was also an absolute requirement; reactions attempted with thiol in place of disulfide gave immediate precipitation of a metal complex, and no sulfide product could be found. Unlike the reaction among 5-(chloromercurio)-2′-deoxyuridine, $Li_2PdCl_4$, and olefins, which results in the reduction of Pd(II) to Pd(0), no Pd(0) formation is observed in the disulfide reaction. At least three known distinct steps are likely to be involved in the overall reaction. First, Pd(II) is known to form complexes with disulfides which are relatively unstable and apparently break down in the presence of nucleophilic solvents to give $\mu^2$ bridging thiolate complexes.[28] Second, palladium must undergo a metal-metal exchange reaction with the 5-(chloromercurio)-2′-deoxyuridine to generate a complex in which palladium is covalently linked at C-5. Finally there must be a step in which the disulfide is cleaved with generation of the C-5 sulfur link and bonding of a thiolate ligand to palladium. This formal process is shown schematically in Scheme II. The actual structures of the intermediates and details of the timing of these events will require further study.

**Acknowledgment.** The National Institutes of Health is gratefully acknowledged for support of this research through NIH Grants AI20480, AI26029, and GM30805. Mass spectral determinations were performed by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant No. CHE 8211164). We gratefully acknowledge NSF Instrument Grant CHE-8509872 for contributing to the purchase of the VXR 300 NMR spectrometer.

**Supplementary Material Available:** Experimental data consisting of reagents and methods and a general procedure for coupling 5-(chloromercurio)-2′-deoxyuridine to disulfide and tables of $^1H$ and $^{13}C$ NMR data (4 pages). Ordering information is given on any current masthead page.

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# A Rhodium Complex That Combines Benzene Activation with Ethylene Insertion. Subsequent Carbonylation and Ketone Formation

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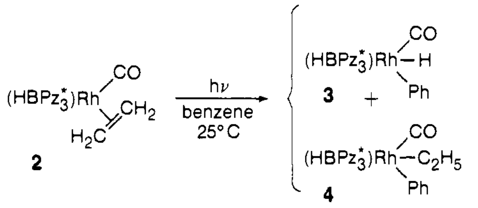
Following our recent report[1] of highly efficient photochemical carbon-hydrogen activation by dicarbonyl{tris(3,5-dimethylpyrazol-1-yl)borato}rhodium(I), $(HBPz^*_3)Rh(CO)_2$ (**1**), we have investigated the derivative $(HBPz^*_3)Rh(CO)(C_2H_4)$, **2**.[2] We now describe a remarkable photochemical reaction of **2** in which benzene activation and insertion of the ethylene ligand are combined to form an ethylphenylrhodium product.[4] We further report the carbonylation of this product and subsequent release of ethyl phenyl ketone.

Ultraviolet irradiation at 25 °C of a degassed benzene solution of **2** (3.6 mM) for 8 min resulted in its complete conversion to **3**[1] and **4**[5] in approximately equal yield (eq 1).[6] Separate ex-



(1)

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[1] Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726-4727.

[2] The new complex **2** was prepared by reaction of $KHBPz^*_3$ with $[(\mu\text{-Cl})Rh(CO)(C_2H_4)]_2$.[3] Data for **2**: IR (*n*-hexane) $\nu_{CO}$ 2013 $cm^{-1}$; $^1H$ NMR ($CD_2Cl_2$, −60 °C, 400 MHz) $\delta$ 5.90 (s, 2 H), 5.60 (s, 1 H), 3.15 (d, 2 H, $J = 8.5$ Hz), 2.33 (s, ~8 H), 2.32 (s, ~6 H), 2.20 (s, 3 H), 2.16 (s, 3 H); MS (16 eV, 90 °C), 456 (7%) $M^+$, 428 (100%) $[M - CO/C_2H_4]^+$, 400 (71%) $[M - CO - C_2H_4]^+$; Anal. ($C_{18}H_{26}BN_6ORh$) C, H, N.

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[4] In a paper which appeared as this manuscript was in preparation (McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246-4262) kinetic evidence was presented for an intermediate $[(\eta\text{-}C_5Me_5)Ir(\eta^2\text{-propene})]$ which oxidatively added benzene and was trapped by phosphine after insertion to produce $(\eta\text{-}C_5Me_5)Ir(PR_3)(Ph)(n\text{-propyl})$. In other related work, benzene activation followed by insertion of an isocyanide ligand into the resulting iron-phenyl bond were proposed as key steps in a catalytic cycle (Jones, W. D.; Foster, G. P.; Putinas, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5047-5048).

[5] Data for **4**: colorless crystals mp 175-178 °C; IR (*n*-hexane) $\nu_{CO}$ 2043 $cm^{-1}$; $^1H$ NMR ($CD_2Cl_2$, ambient, 200 MHz) $\delta$ 7.34 (d, 1 H), 7.13 (t, 1 H), 6.98 (t, 1 H), 6.79 (t, 1 H), 6.58 (d, 1 H), 5.90 (s, 1 H), 5.80 (s, 1 H), 5.79 (s, 1 H), 2.65 (m, 1 H), 2.49 (s, 3 H), 2.48 (s, 3 H), 2.46 (s, 3 H), 2.44 (s, 3 H), 2.20 (m, 1 H), 1.68 (s, 3 H), 1.58 (s, 3 H), 0.69 (t, 3 H, $J = 7$ Hz); MS (16 eV, 100 °C), 534 (32%) $M^+$, 505 (100%) $[M - C_2H_5]^+$, 477 (70%) $[M - C_2H_5 - CO]^+$, 428 (24%) $[M - C_2H_5 - C_6H_5]^+$, 400 (16%) $[M - C_2H_5 - C_6H_5 - CO]^+$. Anal. ($C_{24}H_{32}BN_6ORh$) C, H, N.

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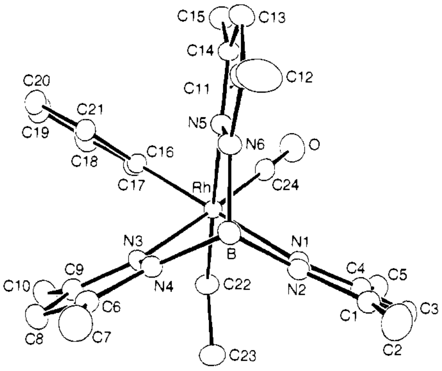
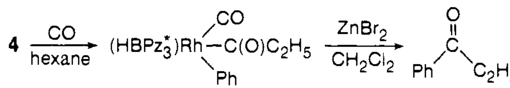


**Figure 1.** Molecular structure of (HBPz*$_3$)Rh(CO)(C$_2$H$_5$)(Ph) (4), viewed approximately along the pseudo-3-fold axis. Selected interatomic distances from Rh to C22, 2.106 (4); C16, 2.053 (4); C24, 1.824 (4); N1, 2.170 (3); N3, 2.104 (3); N5, 2.219 (3) Å. Selected angles: C22-Rh-C24, 86.8 (2); C22-Rh-C16, 90.4 (2); C16-Rh-C24, 86.4 (2); average N-Rh-N, 86.1 (1)°.

periments under the same conditions established that **3** does not react with excess $C_2H_4$ to produce **4** and that **4** is not converted to **3**. Thus one product is not the precursor of the other, and separate pathways (perhaps involving a common intermediate) are indicated. The X-ray crystal structure of **4**[7] (Figure 1) confirms the formulation and demonstrates the high steric demand of the HBPz*$_3$ ligand; the rhodium atom actually lies 0.127 Å above (i.e., on the boron side) the plane formed by the 3-methyl carbons C5, C10, and C15.

When a hexane solution of **4** (3.7 mM) was pressurized with CO at 950 psig and heated at 100 °C for 2 weeks, complete conversion occurred to two carbonylation products **5** and **6**. **5** has been fully characterized[8] as the phenylpropionyl complex (HBPz*$_3$)Rh(CO)(COC$_2$H$_5$)(Ph). While **6** is still under investigation,[9] it converts slowly but completely to **5** in the absence of CO. Thus the complete conversion of **4** to **5** is possible as shown in eq 2.



**5**

(2)

Under conditions so far utilized (maximum 1000 psi at 100 °C) CO pressure does not induce reductive elimination of ketone from **5** or 1,2-diketone from **6**.[10] However, noting the observation[11] that ZnBr$_2$ promoted reductive elimination of RH from Cp*Ir(PMe$_3$)(R)(H), we treated **5** with excess ZnBr$_2$ (CH$_2$Cl$_2$, 25 °C, 4 h) and found that propiophenone was formed in 82% yield. The fate of the rest of complex **5** is not yet known, and carrying out the ZnBr$_2$ reaction under a CO atmosphere did not result in formation of **1**.

The reactions reported here are stoichiometric rather than catalytic, and the key rhodium complex has not been regenerated. Nevertheless, ethylene, benzene, and carbon monoxide have been combined under mild conditions with photochemical assistance to produce propiophenone. We think these reactions provide an encouraging glimpse of the role that C-H activation by transition-metal complexes may play in the manipulation and functionalization of hydrocarbons.

**Acknowledgment.** We gratefully acknowledge the support of this work by the Natural Sciences and Engineering Research Council.

**Supplementary Material Available:** Experimental details for syntheses and reactions with spectroscopic and analytical data for **2**, **3**, **4**, and **5**, tables of positional and thermal parameters, interatomic distances and angles, and details of X-ray crystallographic data collection for **4** (26 pages). Ordering information is given on any current masthead page.

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(6) The reaction also took place in sunlight or incandescent light but more slowly and with some variation in the ratio **3**:**4**.

(7) The X-ray crystallographic study was carried out by Dr. R. G. Ball in the Structure Determination Laboratory of this department. **4** crystallized from hexane in the monoclinic space group $P2_1/n$, $a = 10.752$ (3) Å, $b = 17.591$ (3) Å, $c = 13.751$ (2) Å, $\beta = 104.43$ (2)°, $V = 2519$ Å$^3$, $Z = 4$; 3601 unique reflections having $I > 3\sigma(I)$ were used in the solution and refinement: $R = 0.035$, $R_w = 0.044$.

(8) Data for **5**: colorless crystals mp 184-185 °C; IR (*n*-hexane) $\nu_{CO}$ 2069, 1670 cm$^{-1}$; $^1$H NMR (CD$_2$Cl$_2$, ambient, 200 MHz) $\delta$ 8.24 (d, 1 H), 7.18 (t, 1 H), 6.96 (t, 1 H), 6.74 (t, 1 H), 6.37 (d, 1 H), 5.94 (s, 1 H), 5.84 (s, 1 H), 5.72 (s, 1 H), 2.50 (s, 3 H), 2.46 (s, 3 H), 2.42 (s, 3 H), 2.35 (m, 2 H, C$H_2$), 2.25 (s, 3 H), 1.59 (s, 3 H), 1.29 (s, 3 H), 0.82 (t, 3 H, $J = 7$ Hz); the 400 MHz spectrum established that the $\delta$ 2.35 multiplet was an AB pattern with $\Delta\delta = 0.093$, $J_{AB} = 19$ Hz; MS (16 eV, 150 °C), 533 (100%) [M - C$_2$H$_5$)]$^+$, 505 (25%) [M - C$_2$H$_5$ - CO]$^+$, 477 (73%) [M - C$_2$H$_5$ - 2CO]$^+$, 400 (8%) [M - C$_2$H$_5$ - C$_6$H$_5$ - 2CO]$^+$. Anal. (C$_{25}$H$_{32}$BN$_6$O$_2$Rh) C, H; N: calcd 14.95; found 14.30.

(9) Although **6** has not been obtained free of **5**, $^1$H and $^{13}$C NMR studies by Dr. Glenn J. Sunley have established its probable identity as the benzoyl propionyl complex (HBPz*$_3$)Rh(CO)(COC$_6$H$_5$)(COC$_2$H$_5$).

(10) This is in marked contrast with the reactivity of ($\eta^5$-C$_5$Me$_5$)Rh(CO)(Me)(Ph) with CO, which leads under milder conditions (6 h, 100 °C, 7.5 atm) to acetophenone in 99% yield along with [($\eta^5$-C$_5$Me$_5$)Rh(CO)]$_2$: Sunley, G. J.; Fanizzi, F. P.; Saez, I. M.; Maitlis, P. M. *J. Organomet. Chem.* **1987**, *330*, C27-C30.

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## Synthesis and Electrophilic Reactivity of Dicarbonyl(alkene)(arene)manganese Cations[†]

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A wide variety of nucleophiles add to the arene in (arene)Mn(CO)$_3$$^+$ (**1**) to give exo functionalized (cyclohexadienyl)Mn(CO)$_3$ complexes (**2**).[1-4] Further elaboration of **2** to generate coordinated cis difunctionalized cyclohexadienes has been reported.[5] Herein we report the synthesis and reactivity of (arene)Mn(CO)$_2$(alkene)$^+$ (**3**); it is anticipated that this new class of electrophilic complexes will provide a general route to *endo*-cyclohexadienyl complexes and *trans*-cyclohexadienes.

A good way to prepare **3** is outlined in Scheme I. Treatment of **1** in THF with a slight excess of Me$_3$NO (25 °C, 30 min, N$_2$, dark) leads to ready displacement of CO[6] to give **4** as a purple solid in 80-90% yield after filtration and solvent removal at ≤30 °C. The heat and light sensitive complex **4** can be stored at -10 °C for weeks; its purity was established as typically 90% by dissolution in CD$_3$CN, which rapidly generates free THF (determined by NMR) and (arene)Mn(CO)$_2$(NCCD$_3$)$^+$PF$_6$$^-$. (The complex [(C$_6$Me$_6$)Mn(CO)$_2$MeCN]PF$_6$ was prepared independently and fully characterized by X-ray diffraction.[7]) The THF in **4** is replaced by alkenes to give good yields (≥80%) of **3** as thermally stable yellow-orange salts. The usual procedure with liquid alkenes was to reflux a CH$_2$Cl$_2$ solution of **4** and excess

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[†] Dedicated to the memory of Fred A. Snavely, an inspiring teacher, scholar, and friend.

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