resultant products **8**, **10**, and **12**, with the exception of **8f** and **8i** (see above), were not isolated and were characterized on the basis of ^{31}P NMR data (see Table V).

EHMO calculations[31,33] were carried out on the simplified complexes $\overline{(OC)_4Mo(\mu\text{-}PH_2)_2Pt}(PH_3)$ (**15**), $(CO)_4\overline{Mo(\mu\text{-}PH_2)_2Mo}(CO)_4$ (**16**), and *cis*-$(CO)_4Mo(PH_3)_2$ (**17**) with interatomic distances based on X-ray crystal structure determinations[36,46] with idealized geometries: C_{2v} for **15**, D_{2h} for **16**, and C_{2v} for **17**. The P-H distances were 1.40 Å and ∠MPH = 110° for the PH_3 group, and ∠HPH = 109° for PH_2 groups. Variation of ∠HPH from 109 to 120° did not significantly change the observed trends. Values for H_{ii} and orbital exponents were taken from ref 47.

The formyl complex $[(OC)_3(HCO)\overline{Mo(PH_2)_2Pt}(PH_3)]^-$ was calculated with C—H = 0.95 Å, C═O = 1.33 Å, and ∠MoCH = 117°. The CHO group was rotated around the Mo–C vector in order to find the minimum energy configuration.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Supplementary Material Available: Tables SI–SIV, containing final atomic and thermal parameters of the hydrogen atoms, general temperature factor expressions, bond distances, and bond angles (5 pages); Table SV, containing observed and calculated final structure factors (27 pages). Ordering information is given on any current masthead page.

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(47) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

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Thermal and Photochemical C-H Bond Reactions of Alkenes in (Tris(pyrazolyl)borato)iridium(I) Complexes

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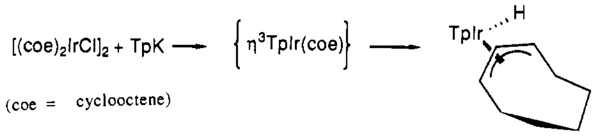
$[Ir(ol)_2Cl]_2$ (ol = cyclooctene or ethylene) reacts with KTp (Tp = hydrotris(1-pyrazolyl)borate) to give, in the cyclooctene case, $TpIr(\eta^3\text{-cyclooctenyl})H$ (**1**) and, in the ethylene case, $TpIr(C_2H_4)_2$ (**2**). Complex **2** reacts with CO at 1 atm and 25 °C to give the known $TpIr(CO)_2$ (**3**) and reacts with excess methyl acrylate (MA) to give $TpIr(C_2H_4)(MA)$ (**5**). On irradiation (350 nm), **2** gives $TpIr(\eta^2\text{-}C_2H_4)H(\eta^1\text{-vinyl})$ (**4**). This appears to take place by intramolecular vinyl C–H bond activation; $\eta^3\text{-}TpIr(C_2H_4)$ is proposed as the key intermediate. In the ^1H NMR spectrum, the ethylene ligands of **2** show a singlet at room temperature for the vinylic protons, but decoalescence takes place at ca. 260 K ($\Delta G_{rot}{}^* = 13$ kcal/mol).

Introduction

Tp complexes (Tp = hydrotris(1-pyrazolyl)borate) were first prepared by Trofimenko[1] in the 1960s, but a number of new applications have only very recently appeared. Graham[2] has shown that compounds of the type $Tp^*M(CO)_2$ (M = Ir, Rh; Tp* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) activate alkanes (RH) on irradiation at 350 nm to give $Tp^*M(CO)H(R)$. Work in our own group on alkane activation[3] has involved a search for degradation-resistant ligands. We wondered whether Tp or Tp* might be suitable and so set out to make examples of polyhydrides, $TpMH_x$, which we hoped might be catalyst precursors for alkane conversions. We have recently reported[4] the first results of this work including the synthesis of $TpReH_6$, which is the first nitrogen-supported polyhydride. None of the Re complexes were catalytically active, and so we moved to Ir. As we will see below, we have not yet been able to prepare complexes of the $TpIrH_x$ type, but we were able to show that such systems would be very unlikely to act as alkane dehydrogenation catalysts. In the course of this work, we came upon a number of interesting and unexpected features of TpIr chemistry, which we report in this paper.

Results

In the hope of obtaining a labile system from which we could prepare the polyhydride, we attempted to make $TpIr(coe)_2$ (coe = cyclooctene) by the route shown in eq 1. In fact, the product turned out to be the cyclooctenyl hydride (**1**). The material is very soluble even in hexane and can be isolated as solvated powder.



1

(1)

The proposed structure is consistent with the high-resolution mass spectrometric data and the ^1H and ^{13}C NMR spectra in toluene-d_8 at 25 °C. The ^1H NMR spectrum shows three sets of resonances for the Tp pyrazole rings, an Ir–H resonance at δ −18.1, and resonances corresponding to the vinylic CH protons of the coordinated cyclooctenyl group at 5.57 (t, 1 H), 4.54 (m, 1 H), and 4.04 ppm (m, 1 H). The J_{app} of 7.9 Hz is comparable to that observed by Faller and Chao[5] in a cyclooctenyl molybdenum complex. We do not observe any coupling between the Ir-H group and any allyl proton, in contrast to the situation in some other allyl hydrides.[6]

An η^3-Tp ligand has a high steric demand. As we shall see, only relatively unhindered olefins will give derivatives of the type $(\eta^3\text{-}Tp)Ir(ol)_2$. This suggests to us that one coe must dissociate before the three pyrazole rings can ligate to the Ir center in eq 1. The intermediate $(\eta^3\text{-}Tp)Ir(coe)$ is related to the type "CpIrL" proposed by Bergman[7] and Graham and their co-workers for the photochemical activation of various C–H bonds. Here the same type of intermediate is formed, and an allylic C–H bond of the coordinated coe is activated to give **1**.

The symmetry of the complex is lower than expected; the three Tp pyrazole rings and the two ends of the allyl group are inequivalent (Figure 1). The molecule therefore lacks a plane of

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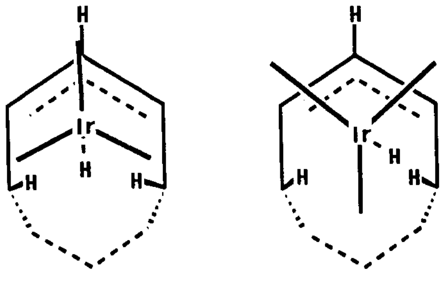


1a **1b**

Figure 1. Conformations **1a** and **1b**.

symmetry (**1a**) but adopts the unsymmetrical structure **1b**. Unfavorable steric interactions between the allyl and the pyrazolyl protons in **1a** but not in **1b** may cause the cyclooctenyl group to tilt. We hoped to observe the coalescence of the allyl resonances by variable-temperature proton NMR spectroscopy, which would happen if equilibration of **1a** and **1b** took place. Unfortunately, **1** decomposes at 60 °C before any line broadening occurs. In toluene-d_8 the major decomposition product is an unidentified hydride having a ^{1}H NMR resonance at δ −26.0. **1** fails to react with hydrogen and decomposes slowly in chlorinated solvents.

To avoid allylic C–H activation in the alkene, we moved to the ethylene analogue TpIr$(C_2H_4)_2$ (**2**; Tp ligands are η^3 unless shown otherwise), which can be prepared in two steps. Reaction of $[Ir(coe)_2Cl]_2$ with ethylene (1 atm, 25 °C) in THF produces a solution of $[Ir(C_2H_4)_2Cl]_2$, which is treated with KTp at 25 °C to give **2**. The colorless product is identified from the microanalytical, ^{13}C NMR, and ^{1}H NMR data. The ^{1}H NMR spectrum shows only one set of pyrazolyl resonances down to 190 K. The ethylene protons decoalesce at ca. 260 K, which implies that ΔG^* for ethylene rotation is 13 kcal/mol.

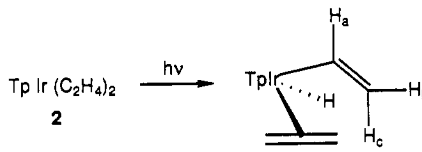
Although **2** fails to react with such potential ligands as hydrogen, Et_3SiH, $(Et_2SiH)_2$, and pyridine, it does react with CO, even at 1 atm and 25 °C, to give the known dicarbonyl TpIr$(CO)_2$ (**3**). This complex has previously been prepared by Graham[2] from TpIr(cod) by carbonylation at >20 atm, but the compound is now available much more conveniently by our route. Complex **2** also reacts with methyl acrylate (MA) at 20 °C or in an acetone/CO_2 bath to give TpIr(C_2H_4)(MA) (**5**). The ^{1}H NMR spectrum shows one set of pyrazolyl resonances down to 223 K. The olefinic protons are broad at 298 K but on cooling to 223 K resolve to seven distinct resonances, suggesting that the product is a mixed-olefin complex. The steric bulk of η^3-Tp may well be responsible for the failure to undergo substitution by a second MA.

TpRh$(C_2H_4)_2$ undergoes substitution reactions at a rate comparable to that observed for the 16e complex (acac)Rh$(C_2H_4)_2$ rather than the 18e analogue CpRh$(C_2H_4)_2$. This has led to speculation that TpRh$(C_2H_4)_2$ might have an η^2-Tp structure even in the ground state.[8] TpIr$(C_2H_4)_2$ fails to react with hydrogen and silanes at room temperature. This suggests that **2** is an 18e species, since we would expect these ligands to react with a 16e form of **2** and lead to the hydrogenation or hydrosilation of the coordinated alkene. The fact that Ir tends to form stronger M–L bonds than does Rh may account for any difference in Tp hapticity between the iridium and rhodium compounds; alternatively the Rh complexes may in fact also have the 18e structure.

C–H Activation Experiments

Although we were unable to make TpIrH_4 itself, we were able to make the cyclooctenyl hydride **1**. Bergman has shown that the analogous Cp*Ir(allyl)H activates alkanes.[6a] We find that both **1** and **2** fail to dehydrogenate cyclooctane under our usual conditions, both at 150 °C and at 50 °C,[3] and this suggests that TpIrH_4 itself would not be a catalyst, since **1** would be the expected intermediate in the dehydrogenation of cyclooctane by TpIrH_4. Both **1** and **2** fail to react thermally even with the more reactive C–H bonds of benzene. The bulk of the η^3-Tp group may be a factor, since steric bulk tends to disfavor intermolecular C–H activation.[9]

On irradiation at 350 nm, the ethylene complex **2** rearranges to the vinyl hydride **4** (eq 2). This product is accompanied by ca. 10% of another hydride from which we have not been able to free it. The identity of **4** is clear from the ^{1}H NMR spectrum. The hydride resonates at −16.6 ppm, and the vinyl protons resonate at 6.75 (H_a), 5.33 (H_b), and 4.50 (H_c) ppm. The H–H coupling constants within the vinyl group (J_{trans} = 17.8, J_{cis} = 10.5, and J_{gem} = 3.2 Hz) are comparable to those reported by Wenzel and Bergman[10d] for Cp*Re$(PMe_3)_2$(CH=CH_2)H.



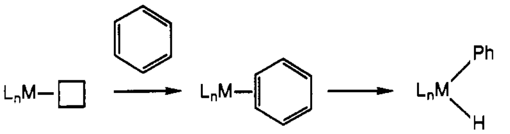
(2)

The reaction of eq 2 is of particular interest as an example of vinylic C–H activation, of which several cases are now known.[10] In all the previous cases, it has been shown that the isolated vinyl hydride photoadduct is the kinetic product, but on warming, this species largely or completely rearranges to the isomeric alkene complex.

In contrast, we do not observe any rearrangement to **2** on refluxing in hexanes or uopn heating to 125 °C in a sealed tube.[11] Compound **4** is quite inert to any substitution chemistry and does not even react with *tert*-butyl isocyanide at 25 °C.

Mechanisms of Vinylic C–H Activation

Vinylic C–H activation has been observed in several systems,[10,12,13] including cases where alkane activation has not been observed. The thermodynamics of oxidative addition of a vinyl C—H bond is probably more favorable than that for an alkane C—H bond; this certainly seems to be the case for arene vs alkane C—H activation.[12] The M—CH=CH_2 bond should be stronger than the M—C_2H_5 bond on both electronic and steric grounds. Metal to ligand π^* back-bonding, at least for a late transition metal such as Ir, should strengthen the bond, and the vinyl group should have a substantially smaller cone angle than the ethyl group. Jones and Feher[12c,d] have demonstrated that precoordination of the substrate to the metal precedes C–H bond activation in the case of arene activation (eq 3). This type of intermediate has not been clearly demonstrated for any alkanes, however.



(3)

Ligands that bear a vinyl group (e.g., 2-vinylpyridine) can give oxidative addition of a vinylic C–H bond[13] in a cyclometalation reaction. In the cases cited[11] there was no evidence for the formation of an η^2-olefin complex prior to the activation step. Vinylic C–H activation has also been seen in many polynuclear systems.[14]

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(8) (a) Trofimenko, S. *J. Am. Chem. Soc.* **1969**, *91*, 588. (b) O'Sullivan, D. J.; Lalor, F. J. *J. Organomet. Chem.* **1974**, *65*, C47–C49. (c) King, R. B.; Bond, A. *J. Organomet. Chem.* **1974**, *73*, 115–118.

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(11) It is important to note that the expected product **2** itself decomposes in cyclooctane at 125 °C in a sealed tube, but we did not find the same decomposition products as in the attempted thermal rearrangement of **4**.

(12) (a) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 843. (b) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113. (c) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240. (d) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650.

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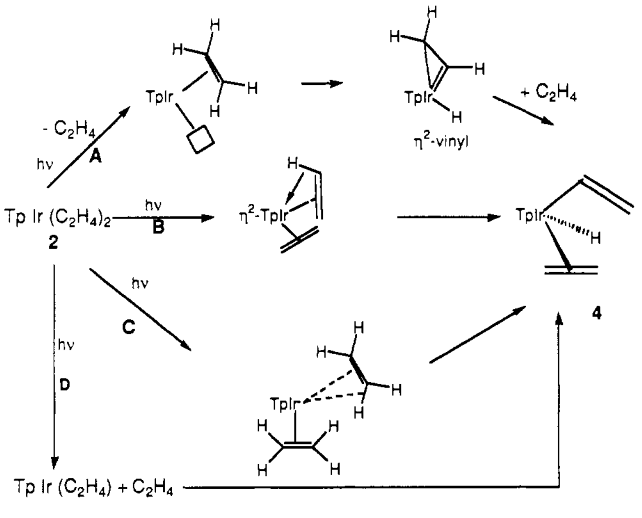
Scheme I. Possible Reaction Pathways for Vinylic C–H Activation by **2**



It has been presumed that an olefin bound to one metal center is activated by a second metal (eq 4 and 5).

$$Re_2(CO)_8(olefin)_2 \rightarrow Re_2(CO)_8(olefin) + olefin \quad (4)$$

$$Re_2(CO)_8(olefin) \rightarrow (\mu\text{-}H)(\mu\text{-alkenyl})Re_2(CO)_8 \quad (5)$$

More recently, both Bergman et al.[10a,d,e] and Field and Baker[10b] have shown that vinylic C–H bond activation need not proceed via prior π complexation. Bergman[10a] has suggested the following mechanism for vinylic C–H activation:

(6)

For our system, there are two possibilities. Either the alkene that is activated is already bound to the metal in the reaction intermediate (mechanisms A–C in Scheme I), or it is the dissociated alkene that is activated (mechanism D in Scheme I). To distinguish between them, we photolyzed **2** in the presence of other olefins (cyclooctene, norbornylene, 3,3-dimethyl-1-butene, and vinyltrimethylsilane). If photolysis liberates ethylene and a free alkene undergoes C–H activation, then we should observe the products of insertion of the added olefins. However, only **4** is obtained. It might be argued that steric differences between ethylene and 3,3-dimethyl-1-butene might favor attack on the former. We feel this only applies to η^2 C=C ligation. If attack were to take place directly on the terminal vinyl C—H, then there should be essentially no difference in steric properties between the two alkenes. We attempted to run the reaction in the presence of C_2D_4, but there is rapid exchange of C_2D_4 with bound C_2H_4 in **2** before photolysis at accessible temperatures (to −78 °C), so we were unable to carry out this confirmatory test. We conclude, however, that a bound olefin undergoes C–H activation; therefore, mechanism D is ruled out.

In mechanism C, the alkene slips over to the η^2-CH form before oxidative addition. This pathway should be independent of added ethylene, but we find that ethylene (1 atm, 90 mol equiv) completely inhibits the reaction without any apparent change in **2**. Mechanism C is therefore ruled out.

Mechanism B is unlikely for several reasons. First η^2-TpIr$(C_2H_4)_2$ is expected to be a square-planar complex, which like the known (acac)Ir$(C_2H_4)_2$[15] should not give C–H activation. In addition, this mechanism should lead to the reaction being zero order in ethylene, in which case the presence of excess ethylene should not inhibit the reaction. One could argue that excess ethylene might produce η^2-TpIr$(C_2H_4)_3$, which could be inactive for insertion into ethylene C–H bonds. The NMR spectrum of **2** is unaffected by excess ethylene, and so the tris(ethylene) complex is not formed thermally. The inhibition is not a general effect of adding a ligand but seems to be specific to ethylene; even in neat acetonitrile-d_3, photolysis of **2** gives **4** as the only hydride.

Mechanism A seems to best fit the observed data because it is the only one that could lead to the observed specific inhibition by ethylene. We have been unable to trap the proposed intermediate, {η^3-TpIr(C_2H_3)H}, with added ligands such as methyl acrylate, C_2D_4, or CO because the starting material, **2**, undergoes rapid exchange with these ligands prior to photolysis. This suggests that a pathway for facile thermal substitution exists. We believe that the light induces ethylene departure; the resulting unstable intermediate η^3-TpIr(C_2H_4) is capable of alkane activation.

Conclusions

Intramolecular vinyl activation of ethylene seems to be involved in the photoconversion of the bis(ethylene) complex **2** to the vinyl hydride **4**. Attempts to make TpIr(coe)$_2$ led to the formation of TpIr(cyclooctenyl)H (**1**) in which steric effects cause the Tp ligand to tilt. TpIr$(C_2H_4)_2$ (**2**) is a useful synthetic intermediate for making TpIr(CO)$_2$ and TpIr(C_2H_4)(MA). The 16e species η^3-TpIr(ol) is probably the intermediate that undergoes intermolecular vinyl C–H activation. The TpIr system is not an effective alkane conversion catalyst possibly because these compounds have low thermal stability.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques. NMR spectra were recorded on a Bruker WM-250 or a JNM-FX 90Q FT spectrometer. IR spectra were recorded on a Nicolet 5-SX FT spectrometer. High-resolution mass spectra (HRMS) were recorded on a Kratos MS-80 RFA spectrometer. Combustion analyses were performed by Galbraith Laboratories. Photolyses were carried out in a Rayonet RMR-500 photochemical reactor with four RPR 3500-Å lamps.

Tetrahydrofuran, ether, toluene, hexanes, and benzene were distilled from sodium benzophenone ketyl. Potassium hydrotris(1-pyrazolyl)borate was prepared by the method of Trofimenko.[16] [(coe)$_2$IrCl]$_2$ was prepared according to Onderdelinden[17] from ammonium hexachloroiridate. Ethylene was purchased from Linde Specialty Gases. C_2D_4 was prepared by dropwise addition of $C_2D_4Br_2$ (MSD Isotopes) to magnesium turnings in ether. Alkanes were purified as previously described.[18]

(Hydrotris(1-pyrazolyl)borato)(η^3-cyclooctenyl)hydroiridium(III) (1). To [(coe)$_2$IrCl]$_2$ (354 mg, 0.395 mmol) and potassium hydrotris(1-pyrazolyl)borate (198 mg, 0.79 mmol) in a dry Schlenk tube was added freshly distilled THF (30 mL). The resultant orange solution was allowed to stir at room temperature for 2 h, during which time it became pale yellow. The THF was removed in vacuo. Hexanes were added, and the solution was filtered over Celite. The hexanes were removed in vacuo, affording a 78% yield of a pale tan powder. ^{1}H NMR (250 MHz, toluene-d_8; s = singlet, d = doublet, dd = doublet of doublets, c = complex resonance): δ 8.15 (d, 1 H, J = 2 Hz), 8.02 (d, 1 H, J = 2 Hz), 7.49 (d, 1 H, J = 2 Hz), 7.45 (d, 1 H, J = 2 Hz), 7.32 (d, 1 H, J = 2 Hz), 7.27 (d, 1 H, J = 2 Hz), 6.08 (t, 1 H), 5.78 (t, 1 H), 5.76 (t, 1 H), 5.57 (t, 1 H, J_{app} = 8 Hz), 4.54 (m, 1 H), 4.04 (m, 1 H), 2.61 (m, 2 H), 2.3–2.1 (m, 2 H), 1.3–1.8 (m, 6 H), −18.10 (s, 1 H). ^{13}C NMR (250 MHz, toluene-d_8): δ 143.9, 142.6, 141.4, 135.2, 135.0, 134.3, 106.24, 105.2, 105.1, 70.2, 63.53, 34–26.5, 14.22. IR (neat, NaCl plates): 2471 cm^{-1} (ν_{B-H}). HRMS: 516 (M + 1). Anal. Calcd for $C_{17}H_{24}N_6BIr(C_4H_8O)_{2.5}$: C, 46.62; H, 6.35; N, 12.07. Found: C, 46.48; H, 6.22; N, 12.00.

(Hydrotris(1-pyrazolyl)borato)bis(ethylene)iridium(I) (2). A suspension of [(coe)$_2$IrCl]$_2$ (500 mg, 0.558 mmol) in freshly distilled THF (20 mL) was degassed (three freeze–pump–thaw cycles). After warming, ethylene was bubbled (1 atm, 20 mL/min) through the solution until it became almost colorless. Meanwhile a degassed solution of potassium tris(pyrazolyl)borate (280 mg, 1.2 mmol) in THF (10 mL) was transferred (canula) into the solution of the iridium complex. The reaction mixture initially turned a deep yellow and then quickly became much

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Inorg. Chem. **1989**, *28*, 3447-3452

lighter. The THF was removed in vacuo and freshly distilled toluene (15 mL added). The solution was then filtered over Celite and concentrated, and hexanes were added to afford a white precipitate (463 mg, 90%), which was filtered and washed with hexanes. ^{1}H NMR (90 MHz, 298 K, CD_2Cl_2): δ 7.81 (d, 3 H), 7.71 (d, 3 H), 6.26 (t, 3 H), 2.07 (s, 8 H). ^{1}H NMR (250 MHz, CD_2Cl_2, 218 K): 7.81 (d, 3 H), 7.71 (d, 3 H), 6.26 (t, 3 H), 2.37 (d, 4 H), 1.61 (d, 4 H) (coalescence ca. 263 K). ^{13}C NMR (250 MHz, CD_2Cl_2, 298 K): δ 139.68, 135.59, 105.85, 29.48. IR ($CHCl_3$): 2478 cm^{-1} (ν_{B-H}). Anal. Calcd for $C_{13}H_{17}BIrN_3$: C, 33.84; H, 3.90; N, 18.21. Found: C, 33.86; H, 3.98; N, 17.35.

(Hydrotris(1-pyrazolyl)borato)dicarbonyliridium(I) (3). Carbon monoxide (1 atm, 20 mL/min) was passed into a THF (10 mL) solution of **2** (78 mg) for 5 min. The THF was removed in vacuo to give a bright yellow solid in quantitative yield identified as **3** by comparison to the spectral properties previously reported.[2] ^{1}H NMR (250 MHz, toluene-d_8): δ 7.45 (d, 3 H), 7.29 (d, 3 H), 5.79 (t, 3 H). IR (Nujol mull): 2485 cm^{-1} (ν_{B-H}); 2084, 2055, 1999, 1978 cm^{-1} (ν_{CO}). IR (heptane): 2074, 2049, 2009, 1974 cm^{-1} (ν_{CO}).

(Hydrotris(1-pyrazolyl)borato)(ethylene)hydro(η^1-vinyl)iridium(III) (4). An ether or acetone solution of **2** (25 mg) in a Pyrex Schlenk tube or borosilicate NMR tube was photolyzed for 2 h at 350 nm. The major product (ca. 90%) was the title vinyl hydride, which was identified by its spectral properties but could not be further purified. ^{1}H NMR (250 MHz, acetone-d_6): δ 7.95–7.4 (m, 6 H), 6.75 (dd, 1 H), 6.34 (t, 1 H), 6.28 (t, 1 H), 6.25 (t, 1 H, J_{app} = 2 Hz), 5.33 (dd, J_{cis} = 10.5 Hz, 1 H, J_{gem} = 3.2 Hz, 1 H), 4.50 (dd, 1 H, J_{trans} = 17.8 Hz), 3.24 (c, 2 H), 2.84 (c, 2 H), −16.57 (s, 1 H); observable resonances of minor product δ 7.8–7.0 (m, 6 H), 6.4–6.3 (m, 3 H), 3.5 (c, 2 H), 3.0 (c, 2 H), −17.16 (s, 1 H).

(Hydrotris(1-pyrazolyl)borato)(ethylene)(methyl acrylate)iridium(I) (5). A dry Schlenk tube was charged with **2** (103 mg, 0.22 mmol), methyl acrylate (43 μL, 0.48 mmol), and THF (10 mL), and this mixture was allowed to stir at 20 °C for 3 h. THF was removed in vacuo. The residue was recrystallized from ether and hexanes to give **5** (95%). ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ 7.73 (d, 3 H), 7.66 (d, 3 H), 6.23 (t, 3 H), 3.62 (s, 3 H), 3.13 (b, 1 H), 2.19 (b), 2.26 (c, 1 H), 2.21 (dd, 1 H). ^{1}H NMR (223 K): δ 7.73 (d, 3 H), 7.66 (d, 3 H), 6.23 (t, 3 H), 3.82 (t, 1 H), 3.64 (s, 3 H), 3.06 (dd, 1 H), 2.86 (t, 1 H), 2.74 (t, 1 H), 2.6–2.4 (c, 2 H), 2.11 (t, 1 H). ^{13}C NMR (250 MHz, $CDCl_3$, 298 K): δ 177.4, 138.9, 135.2, 105.5, 50.6, 49.8, 49.7, 14.0, 13.8. IR ($CHCl_3$): 2483 (ν_{B-H}), 1696 cm^{-1} ν_{CO}. Anal. Calcd for $C_{15}H_{20}BN_6O_2Ir$: C, 34.69; H, 3.88; N, 16.17. Found: C, 33.24; H, 3.85; N, 15.46.

Attempted Alkane C–H Activation. (a) Reaction of 1 with Alkanes above the Decomposition Temperature of 1. A resealable glass pressure vessel charged with **1** (22.5 mg, 0.043 mmol), 3,3-dimethyl-1-butene (0.4 mL, 4.1 mmol), and cyclooctane (1.5 mL) was degassed and filled with argon. The tube was then heated in an oil bath at 150 °C for 12 days, keeping the liquid in the vessel below the surface of the oil and the base of the vessel above the floor of the oil bath. The volatiles were then separated from the organometallic fraction by vacuum transfer. Analysis by the method of Burk and Crabtree[19] showed that only 0.02 mmol of cyclooctene was present.

(b) Reaction of 1 with Alkane below the Decomposition Temperature of 1. A resealable glass pressure vessel charged with **1** (24 mg, 0.047 mmol) and methylcyclohexane (2 mL) was degassed, filled with argon, and heated at (50 °C for 20 h). No olefin was formed, and the ^{1}H NMR spectrum showed **1** was largely unchanged.

(c) Reaction of 1 with Benzene. A resealable glass pressure vessel charged with **1** (21 mg, 0.04 mmol), triphenylphosphine (10 mg, 0.04 mmol), and benzene (1.5 mL) was degassed, filled with argon, and heated (60 °C for 20 h). The ^{1}H NMR spectrum showed only **1** and triphenylphosphine.

(d) Reaction of 1 with Hydrogen. Neither bubbling hydrogen at 1 atm through a solution of **1** nor heating **1** to 42 °C in 1 atm of hydrogen in a resealable glass pressure vessel affords any reaction.

(e) Reaction of 2 with Alkane. A resealable glass pressure vessel charged with **2** (9 mg, 0.02 mmol) and cyclooctane (1.5 mL) was degassed, filled with argon, and heated (70 °C for 18 h). No cyclooctene was formed, and the ^{1}H NMR spectrum showed decomposition products.

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Six-Nitrogen Macrocyclic Complexes of the Dioxouranium(VI) and Praseodymium(III) Ions

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The Schiff-base condensation of 2,6-diacetylpyridine and 1,2-diaminobenzene in the presence of uranyl salts produced complexes of the general formula $[UO_2(C_{30}H_{26}N_6)]X_2$, with X = ClO_4^-, NO_3^-, and CH_3COO^-. A related complex, $[Pr(NO_3)_2(CH_3OH)(C_{30}H_{26}N_6)](ClO_4)\cdot 0.5CH_3OH\cdot 0.5H_2O$, was obtained from a similar metal-templated reaction followed by partial anion metathesis. The Pr(III) complex crystallized in the monoclinic space group $P2_1/c$ with $Z = 4$ in a cell having a = 20.198 (3) Å, b = 14.208 (2) Å, c = 12.727 (2) Å, and β = 104.25 (4)°. In this complex the Pr(III) ion was 11-coordinated, being linked to the six nitrogen atoms of an 18-membered macrocyclic ligand, to two bidentate nitrates situated on opposite sides of the macrocycle, and to one molecule of methanol. A noncoordinated ClO_4^- ion balanced the cationic charge of the complex cation; clathrated water and methanol were also present. The macrocyclic cations existing in these uranyl and praseodymium(III) complexes retained their identity in solution and were moderately inert to metal release in the presence of acids or bases.

Introduction

The condensation of 2,6-diacetylpyridine and 1,2-diaminobenzene was first studied by Stotz and Stoufer,[1] who reported the formation of a yellow crystalline product, $C_{30}H_{26}N_6$, formulated as an 18-membered macrocyclic ligand with a six-nitrogen donor cavity, L_I (Figure 1). These authors also reported a dark brown copper(II) product, $[Cu_2(C_{30}H_{26}N_6)](NO_3)_4$, which they considered to be a dinuclear complex of the same ligand, involving Cu–Cu interactions. Reinvestigation of these species by Nelson et al.[2] showed the yellow compound $C_{30}H_{26}N_6$ to have the tricyclic

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