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Parahydrogen Induced Polarization and the Oxidative Addition of Hydrogen to Iridium Tribromostannyl Carbonylate Anions

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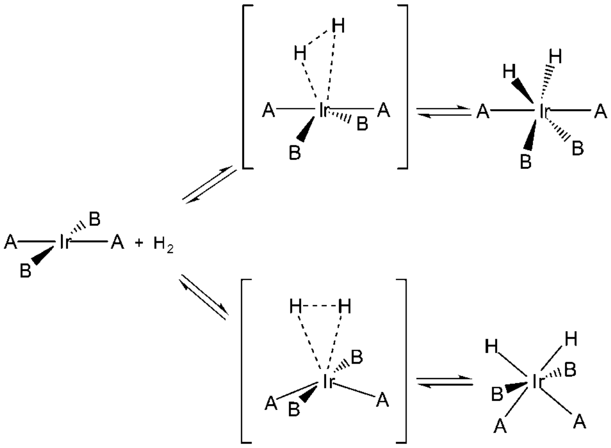
Activation of dihydrogen by a system composed of $(Bu_4N)[IrBr_2(CO)_2]$ (**1**) and tin dibromide in varying ratios was studied using parahydrogen induced polarization (PHIP) which allows the detection of transient dihydrides not observable in conventional ^1H NMR spectra. While the oxidative addition of dihydrogen to neutral and cationic Ir(I) species is common, there are only a few examples of H_2 addition to anionic complexes. Tin dibromide reacts with iridium(I) complex **1** in acetone forming equilibrium mixtures of *cis*- and *trans*-tribromostannyl derivatives $[IrBr_n(SnBr_3)_{2-n}(CO)_2]^-$, $n = 0,1$, the existences of which are inferred from the stereochemistries of the dihydrogen addition products determined using PHIP. The σ-donating effect of the $SnBr_3^-$ ligand facilitates the oxidative addition to the iridium center. The structures of the dihydrides formed upon addition of dihydrogen are assigned on the basis of hydride chemical shifts and values of $^2J(^1H-^{117,119}Sn)$. The only dihydride observed in conventional ^1H NMR spectra is *cis*-*trans*-*cis*-$[IrH_2(SnBr_3)_2(CO)_2]^-$, the identity of which was confirmed using the ^{13}C labeled Ir(I) precursor. Both $[IrBr_2(CO)_2]^-$ and its tribromostannyl derivatives catalyze cis-pairwise addition of dihydrogen to phenylacetylene.

Introduction

The activation of hydrogen by d^8 iridium(I) complexes is known to proceed via a concerted oxidative addition to yield a cis dihydride product.[1−7] This reaction has been extensively studied, both experimentally and theoretically, because of its fundamental importance in hydrogenation catalysis.[4,6,7] In the course of the many investigations, the stereoselectivity of the reaction has been probed, because concerted addition to a square planar complex of D_{2h} or lower symmetry will yield two different isomers, as illustrated in eq 1, and the basis of such selectivity has both steric and electronic components.[5,8−11] In eq 1, hydrogen adds parallel to one of the axes of the square planar complex (i.e., A−M−A or B−M−B) leading to mutually cis hydride ligands, each trans to one of the ligands formerly defining that axis.



(1)

One of the most compelling ways of studying H_2 oxidative addition is by parahydrogen induced polarization (PHIP) in

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the NMR spectrum of the reaction solution.[12−15] Parahydrogen is one of two spin isomers of dihydrogen and corresponds to the nuclear spin “singlet”. PHIP can be observed if hydrogen enriched in the para spin state adds to a metal complex or an organic substrate in a pairwise manner such that spin correlation is maintained between the two transferred protons that originate from the same H_2 molecule.[16−18] If longitudinal relaxation of these protons is not much faster than the rate of hydrogen addition, then non-Boltzmann populations in the proton spin states can result, leading to enhanced absorption and emission lines in the product NMR spectrum. Signal enhancements of up to 1,000-fold have thus been seen.[19,20] Normally, it is assumed that, for observation of PHIP, the transferred protons in the dihydrogen addition products must be magnetically distinct and have an observable scalar coupling to each other. Nevertheless, a somewhat weaker effect has been reported recently for products having equivalent hydrides.[20,21] Several recent reviews and articles discuss various aspects of parahydrogen induced polarization in detail including product operator formulations to facilitate analysis of the spin physics of PHIP.[14,15,18,21,22] To date, PHIP has been used to provide direct evidence of pairwise addition of H_2 to iridium, rhodium, platinum, ruthenium, and tantalum complexes.[12,14,15,18] The signal enhancing ability of PHIP has also allowed for the observation of previously undetected species, including low concentration reaction intermediates, while the normal couplings seen in the PHIP-enhanced resonances involving other nuclei in the complex have permitted detailed structural assignments of these species.[20,23−27]

In the development of group 8 homogeneous catalysts for hydrogenation and hydroformylation, the addition of stannous halides as activators has been extensively examined.[28,29] The addition of SnX_2 leads to the generation of SnX_3^- ligands that are both good σ-donors and strong π-acceptors. The nature of the bonding between the group 8 metal ions and the trihalostannyl ligands has been examined by different spectroscopic methods including heteronuclear NMR spectroscopy.[29−33] The introduction of the trihalostannyl ligands into the coordination sphere of group 8 metal complexes changes, sometimes dramatically, their reactivity and catalytic properties, activating them to oxidative addition and ligand substitution reactions. In the hydroformylation reaction, tin halides can also act as Lewis acids, coordinating to the O atom of acyl intermediates to increase their reactivity.[34] Platinum complexes activated by tin dihalides are well-known catalysts for hydrogenation and hydroformylation of unsaturated compounds,[35−44] while rhodium(I) phosphine complexes containing trichlorostannyl ligands are active catalysts for alkane activation and alkene isomerization.[45] A rhodium−trichlorotin monohydride complex is also known to be an active catalyst for 2-propanol dehydrogenation.[46]

In the present study, PHIP is used to examine H_2 oxidative addition to Ir(I) anionic complexes having carbonyl and tribromostannyl ligands. The particular Ir(I) complexes are generated in situ by the addition of $SnBr_2$ to $IrBr_2(CO)_2^-$ (**1**). The facile exchange of ligands in these anionic Ir(I) carbonyl anions renders isolation of each Ir(I) species impossible, but the H_2 addition chemistry studied in conjunction with PHIP permits inference of their presence and elucidation of the stereoselectivity of H_2 addition to each.

Results

The addition of $SnBr_2$ to oxygen-free acetone solutions of $IrBr_2(CO)_2^-$ (**1**) in varying amounts leads to the in situ formation of different iridium(I) tribromostannyl carbonylate complexes. Because of facile ligand exchange, the individual

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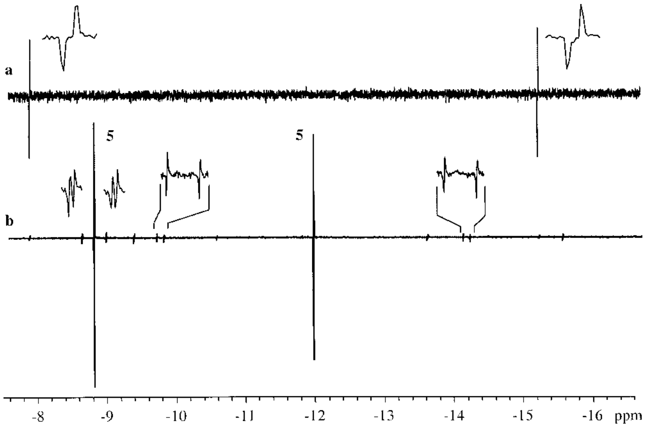
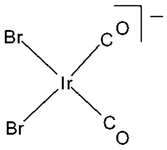


Figure 1. PHIP ^1H spectra of the $(Bu_4N)[IrBr_2(CO)_2]$ (**1**)$-SnBr_2$ system in acetone-d_6 at room temperature and short reaction times: (a) no $SnBr_2$ added; (b) 0.5 mol equiv of $SnBr_2$.

Ir(I) complexes could not be isolated, but their existence is established as a result of the PHIP studies described later that permit unequivocal assignment of product hydride structures. The ratios of $SnBr_2$:**1** used in the different reactions were 0.5:1, 1:1, 2:1, 3:1, and 6:1. In all cases, the addition of $SnBr_2$ proceeds with initial formation of a deep violet-blue color followed by slow conversion to red. The violet-blue color is thought to arise from initial stannous bromide attack and formation of $Ir-Br-SnBr_2$ species, while the red coloration develops from conversion to the tin-coordinated tribromostannyl ligand. On the basis of the assumption of eq 1 involving cis concerted H_2 addition and the identities of the hydride products, the specific Ir(I) tribromostannyl complexes are shown as cis and trans isomers of **2** and **3**. For each ratio of $SnBr_2$:**1**, the reaction solution was allowed to stand overnight, leading to an equilibrium distribution of species for that system.



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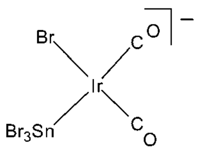

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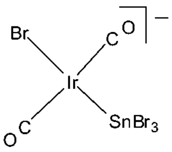
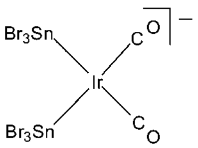
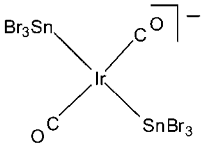


2-trans



3-cis



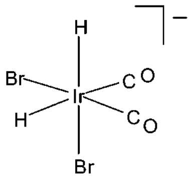
3-trans

In the absence of $SnBr_2$, **1** reacts with para-enriched H_2 to yield the PHIP spectrum shown in Figure 1a. Simple antiphase polarization of the two hydrides of $IrH_2Br_2(CO)_2^-$ (**4**) at δ −7.801 and −15.127 is seen, the former being trans to CO and the latter trans to bromide. The polarization is similar to that reported for $IrH_2I_2(CO)_2^-$ with the antiphase resonances being in the order E/A.[47] The formation of **4** is reversible, and polarization decays slowly on standing. When normal H_2 is used for reaction with **1** under the same conditions, no hydride signals are observed, indicating that the dihydride product **4** is present in very low equilibrium concentration.

Table 1. Parameters of ^1H NMR Spectra of the Iridium(III) Dihydride Complexes **4**−**11**[a]

complex	δ H, ppm	$J(^{119,117}Sn-H)$, Hz	$J(H-H)$, Hz
4[b]	−7.801		−5
	−15.127		
5	−8.676	135.0; 141.5	−1.8
	−11.913	1719.9; 1805.7	
6	−9.277	126.9; 122.5	−5.4
	−16.930	160.8; 153.5	
7	−13.582	1338.6; 1279.1	−4.8
	−17.288	99.6; 95.0	
9	−10.714	117.3; 105.5 1109.7; 1057.1	−3.8
	−12.961	113.6; 101.4 122.3; 116.2	
10	−12.866	996.5; 953.2 93.0; 91.4	−2.2
11[c]	−11.126	95.2; 91.4	

[a] Solution in acetone, 0.014 M of **1** and $SnBr_2$, 340 K. [b] No $SnBr_2$ added; spectra were taken at 317 K. [c] Parameters for labeled compound (used in simulations): mono-labeled **11** (323 K, 0.014 M of **1** and 0.048 M of $SnBr_2$ in acetone-d_6), δ H −11.121 ppm (trans to ^{13}C with $^2J_{HC} = 34.7$ Hz), δ H −11.128 ppm (cis to ^{13}C with $^2J_{HC} = -5.8$ Hz), $^2J_{HH} = -4.2$ Hz; bis-labeled **11** (313 K, 0.002 M of **1** and 0.006 M of $SnBr_2$ in acetone-d_6), δ H −11.117 ppm, $^2J_{CC} = \pm 2.8$ Hz, $^2J_{HC} = 34.7, -5.8$ Hz, $^2J_{HH} = -4.2$ Hz.



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H_2 Addition to Bromo Tribromostannyl Ir(I) Species. The addition of 0.5 equiv of $SnBr_2$ to an acetone solution of $IrBr_2(CO)_2^-$ leads to the in situ generation of mixed bromo tribromostannyl complexes and the PHIP spectrum shown in Figure 1b. Table 1 summarizes the chemical shift and coupling constant data for all of the hydride complexes reported in this paper. While polarized hydride resonances for **4** are discernible, the major polarizations are seen for bromo tribromostannyl complex **5** in which the $^1H-^{117,119}Sn$ couplings (7.6% and 8.6% natural abundances, respectively) allow for unambiguous structural assignment. Specifically, the resonance at δ −11.913 exhibits $^{117,119}Sn$ satellites indicative of the stannyl ligand being trans to the hydride, while the resonance at δ −8.676 shows cis $^{117,119}Sn$ couplings and a chemical shift characteristic of the hydride being trans to CO. (The ratios of the J_{Sn-H} coupling constants for ^{117}Sn and ^{119}Sn are equal to the ratio of the magnetogyric ratios of 0.956 for the two tin isotopes.) On the basis of the fact that **5** is the only tribromostannyl species observable at 295 K and short reaction times, it is possible to assign **5** as the kinetic isomer for H_2 oxidative addition to the mixed bromo

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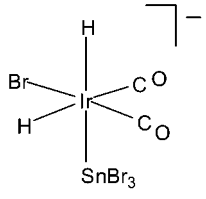
tribromostannyl complex **2-cis**.



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At ratios of $SnBr_2$/**1** of 1:1 and 2:1, essentially the same PHIP spectrum is obtained at 295 K upon short exposure to parahydrogen or after the sample is removed from the spectrometer, shaken, and reinserted into the probe within 30−45 s. The single-pulse acquisitions all reveal that polarized signals from **5** are the major spectroscopic features, while the signals for **4** get extremely weak, and new but weak signals are seen for other hydride products. At a 3:1 ratio of $SnBr_2$/**1**, the system does not yield detectable PHIP signals at room temperature and short exposure times to the para-enriched H_2 atmosphere, but upon raising the temperature to 323 K and higher, polarized signals of all three possible bis(tribromostannyl) dihydrides are seen (vide infra). This observation indicates that at 3:1 and higher ratios of $SnBr_2$/**1**, virtually all iridium(I) is converted into bis(tribromostannyl) derivatives which appear to be less active kinetically in the oxidative addition of dihydrogen than are the mixed bromo tribromostannyl complexes, possibly because of the greater π-acidity of the stannyl ligands. Additionally, excess $SnBr_3^-$ in solution may lead to formation of coordinatively saturated pentacoordinate tris(tribromostannyl) derivatives similar to previously reported species for other platinum metal systems.[48−50]

As the temperature of the reaction system for $SnBr_2$/**1** ratios of 0.5:1 to 2:1 is increased from 45 to 75 °C, polarized signals for two other bromo tribromostannyl dihydrides grow in while the polarization for **5** declines, as shown in Figure 2a. As with **5**, the structures of these hydrides are assigned on the basis of hydride chemical shifts and J_{Sn-H} coupling constants (see Table 1), and a $^1H-^1H$ COSY spectrum was used to confirm the pair of hydrides for each species. For **6**, both hydride resonances exhibit tin satellites consistent with cis hydride−stannyl arrangements and chemical shifts indicative of one hydride being trans to CO (δ −9.277) and the other being trans to Br (δ −16.930). The other dihydride is **7** which is seen in strong polarization. For **7**, the hydride chemical shifts of δ −13.582 and −17.288 and J_{Sn-H} coupling constants indicate that the hydrides are trans to $SnBr_3^-$ and Br^-, respectively, leaving the two carbonyl ligands to be mutually trans. In light of the strong polarization exhibited by **7**, its formation most likely occurs by H_2 oxidative addition to **2-trans** with the axis of addition defined by Br−Ir−$SnBr_3$. An alternative proposal for the formation of **7** by isomerization of **5** appears less probable because the growth of **7** is relatively slow under the conditions when the formation of **5** is fast.

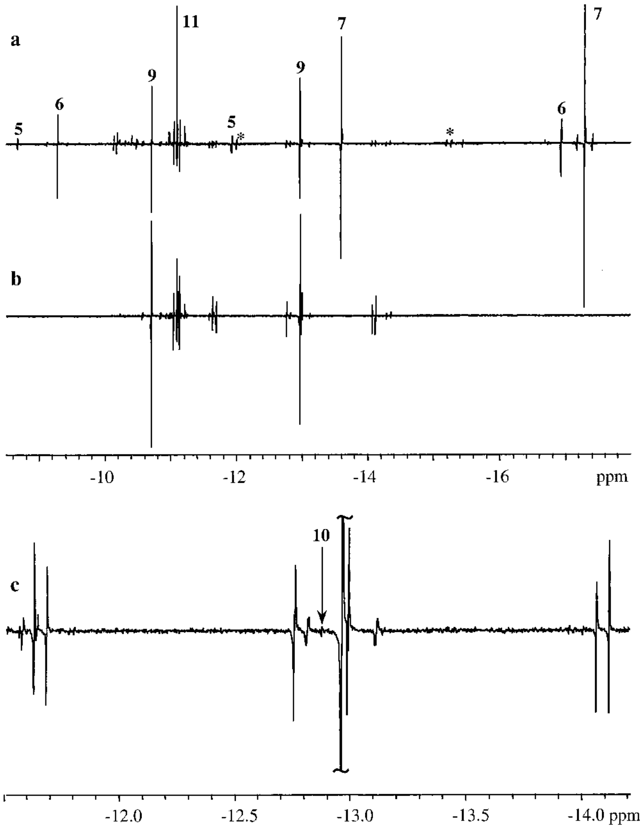
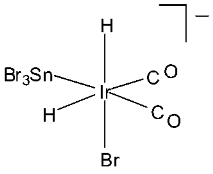


Figure 2. PHIP ^1H spectra of the $(Bu_4N)[IrBr_2(CO)_2]$ (**1**)−$SnBr_2$ system in acetone-d_6 at elevated temperatures and prolonged reaction times: (a) $SnBr_2$/**1** ratio of 1:1 at 68 °C after 5 min; (b) $SnBr_2$/**1** ratio of 3:1 at 85 °C after 2 min; (c) expansion of the spectral region of $^{117,119}Sn$ satellites of **10** with an arrow indicating the middle point of satellite system.

In considering the oxidative addition of H_2 to **2-trans** by the concerted addition mechanism of eq 1, one other dihydride is possible but is not seen. This dihydride, shown as **8**, would form by H_2 addition along the OC−Ir−CO axis and would be PHIP inactive because the two hydrides are magnetically equivalent. While ^{13}C isotopomers of **8** would correspond to an unsymmetrical ABX system and therefore be PHIP active, efforts to observe **8** using ^{13}C-labeled **2** have proven unsuccessful, suggesting that this specific path for H_2 addition is not followed. On the other hand, prolonged shaking of a sample under a normal hydrogen atmosphere produces resonances which may be attributable to **8**, but low signal intensity and an inability to see $^1H-^{117,119}Sn$ couplings with certainty precludes definitive assignment. The possible signals for **8** without polarization suggest formation by a path not involving H_2 addition to **2-trans** such as by tribromostannyl dissociation or $SnBr_2$ elimination from the bis(tribromostannyl) dihydride **11** described later.



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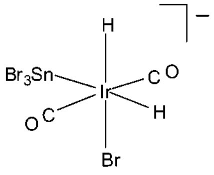

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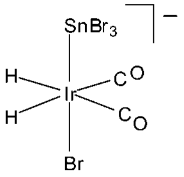

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H_2 Addition to Bis(tribromostannyl) Ir(I) Species. For a 2:1 $SnBr_2$/**1** ratio, reaction with para-enriched hydrogen at 50−60 °C leads to a PHIP spectrum in which polarized hydrides corresponding to both bromo tribromostannyl and bis(tribromostannyl) complexes are seen (Figure 2a). Similar sets of resonances are observed in other experiments with a 1:1 $SnBr_3$/**1** ratio in the same temperature range, but with different relative intensities. The results suggest that extensive and facile scrambling of the stannyl ligands is occurring among the different iridium species. When the $SnBr_2$/**1** ratio is increased to 3:1, however, all of the signals corresponding to bromo tribromostannyl dihydrides disappear, and only the resonances for three isomeric bis(tribromostannyl) dihydrides are detected as shown in Figure 2b and summarized in Table 1.

The most intense resonances of Figure 2b are at δ −10.714 and −12.961 with the former showing coupling to two distinct cis tin nuclei and the latter coupled to both cis and trans $SnBr_3^-$ ligands. The chemical shift of the δ −10.714 resonance is consistent with the hydride being trans to CO and thus allows assignment of the structure of this product as **9**. Complex **9** forms by the oxidative addition of H_2 to **3-cis** and is the only species that would be generated by a cis concerted addition to this Ir(I) species.

The second dihydride species has structure **10** and is identified by its ^{117,119}Sn satellites. For spin-inactive Sn nuclei, the hydrides in **10** are magnetically equivalent and not observable using PHIP. However, when either a ^{117}Sn or ^{119}Sn nucleus is present, the symmetry of the system is lifted and polarized hydride resonances can be seen as the ^{117,119}Sn satellites. From the satellites, which are found with both cis and trans couplings to the hydrides, it is possible to center the resonance of **10** at δ −12.866. Formation of **10** occurs by H_2 addition to **3-trans** with dihydrogen oriented parallel to the axis defined by Sn−Ir−Sn.

The third bis(tribromostannyl) dihydride is **11**, and it forms by addition to **3-trans** with H_2 aligned along the OC−Ir−CO axis. The hydrides for **11** are magnetically equivalent and not subject to parahydrogen enhancement, even with spin-active Sn nuclei. While the hydride resonance of **11** is observed with normal or unpolarized intensity as a singlet at δ −11.126, establishment of its structure is based on polarized signals seen using ^{13}CO because ^{13}C-coupled hydride resonances in **11** will exhibit PHIP. The results are shown in Figure 3. The resonance shown in part a corresponds to the normal or thermal signal of **11** obtained from 128 scans upon long standing of the solution under normal hydrogen. The signals arising from **10** are not observable under these conditions, owing to a much lower concentration. In PHIP spectra of 3:1 $SnBr_3$/**1** with the latter at natural ^{13}C abundance, the hydride of **11** appears as a combination of the thermal signal and parahydrogen enhanced ^{13}C satellites (Figure 3b). To prove this assertion unambiguously, two ^{13}C-labeled samples were examined, one being 14 mM in Ir(I) and the other 2 mM in Ir(I) following dilution with acetone. Both samples were treated with ^{13}CO overnight and then with para-enriched hydrogen. The resulting PHIP spectra are shown as spectra c and d in Figure 3 with the ^{13}C-coupled hydride signals of **11** strongly enhanced.

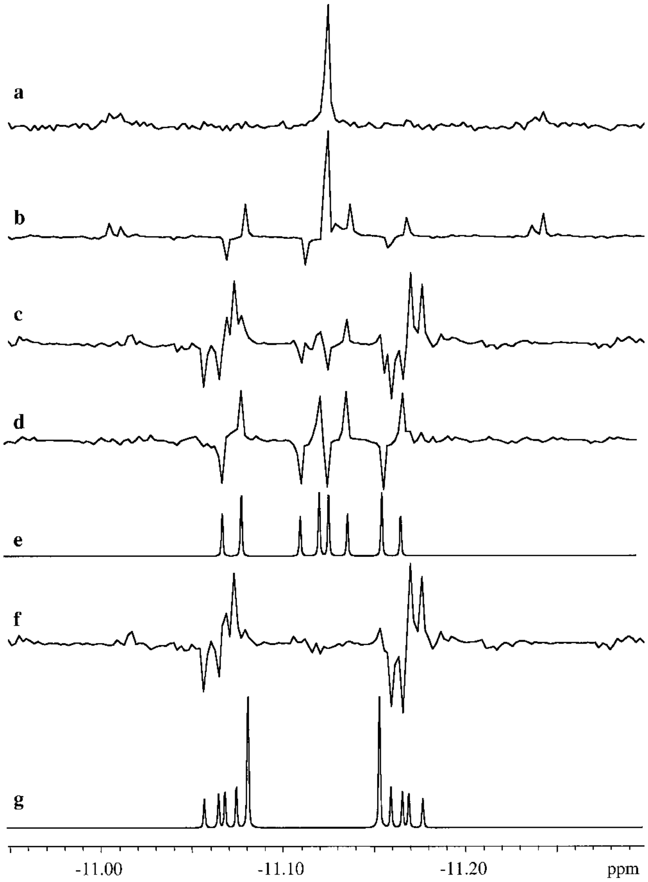

Figure 3. NMR spectra of the hydride of complex **11** under different conditions of measurement and NMR simulation: (a) spectrum at 50 °C under normal hydrogen, 14 mM concentration, 128 pulses; (b) PHIP spectrum of **11** having natural abundance of ^{13}C; (c) PHIP spectrum of a mixture of mono- and bis-^{13}CO labeled **11** at 50 °C, 2 mM concentration, 1 pulse; (d) PHIP spectrum of mono-^{13}CO labeled **11** at 50 °C, 14 mM concentration, 1 pulse; (e) NMR simulation of mono-labeled **11** (of spectrum c); (f) difference spectrum of (b) − (c) yielding the expected pattern for bis-^{13}CO labeled **11**; (g) NMR simulation of bis-^{13}CO labeled **11**.

In the 14 mM sample, only monosubstitution of ^{13}CO into **11** is seen because of the high concentration of complex relative to ^{13}CO present (Figure 3d). Simulation of the ABX system of singly labeled ^{13}CO−**11** shown in Figure 3e agrees with the experimental spectrum, taking into account that H−H coupled doublets are antiphase with the lower-field line in emission. In the dilute 2 mM sample, a mixture of mono- and bis-^{13}CO-labeled dihydrides was obtained, leading to the spectrum shown as Figure 3c that was deconvoluted by subtraction of the spectrum of mono-^{13}CO-labeled **11** from that of the mixture to give the resonances of the bis-^{13}CO-labeled dihydride (Figure 3f). The spectrum of **11** having two ^{13}CO ligands was simulated as a normal AA′XX′ spin system with the same values of J_{HH} and J_{HC} coupling constants as seen in Figure 3g. The two most intense lines in the simulated spectrum are not seen in the PHIP spectrum as they correspond to degenerate transitions with no H−H

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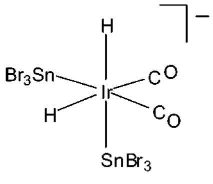
coupling and therefore cancellation of enhanced absorption and emission intensities, while the other resonances correspond to the experimentally observed antiphase doublets, separated approximately by the coupling constant difference (J_{C-H}trans − J_{C-H}cis) and J_{C-C} coupling.[51]



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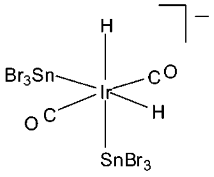

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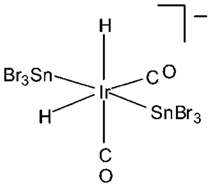

11

Hydrogenation of Alkynes Catalyzed by Iridium−Tin Systems. The Ir−Sn system composed of $[IrBr_2(CO)_2]^-$ (**1**) and $SnBr_2$ was tested for catalytic activity in the hydrogenation of phenylacetylene using para-enriched hydrogen. The reaction proceeds at 55 °C yielding styrene as the hydrogenation product. Polarization in the olefinic resonances at δ 6.75 and 5.17 ppm agrees with what has been reported previously[13,52,53] and indicates that PHIP arises from cis-addition of parahydrogen to the phenylacetylene triple bond. The δ 6.75 and 5.17 ppm resonances exhibit H−H coupling of ∼10.7 Hz as antiphase doublets, indicating that they are cis olefinic protons corresponding to the former parahydrogen nuclei. The remaining olefinic proton of the styrene product is cis to the phenyl group and resonates at δ 5.78 ppm. This proton was initially part of the phenylacetylene substrate and shows a coupling of 17 Hz with the proton trans to it at δ 6.75. The polarization seen in the δ 5.78 resonance is much weaker than that of the other olefinic protons and of opposite phase and arises from polarization transfer by a dipolar relaxation mechanism. Both 1:1 and 2:1 $SnBr_2$/**1** systems, as well as **1** alone, are active as hydrogenation catalysts of phenylacetylene, but catalytic activity is distinctly reduced for Sn/**1** ratios of 3 or greater.

Discussion

Formation of Iridium(I) Species and Scrambling of $SnBr_3^-$ Ligands. The Ir(I) complex $IrBr_2(CO)_2^-$ (**1**) only exists as the cis isomer owing to the strong trans effect and π-acidity of the carbonyl ligands and the complementary π-donation of the bromide ligands. The reaction of **1** with $SnBr_2$, however, leads to both cis and trans isomers of the mono- and bis(tribromostannyl) complexes. The formation of these complexes occurs with extensive scrambling and results in mixtures of **1** and both mono- and bis(tribromostannyl) complexes **2** and **3** for ratios of $SnBr_2$/**1** ranging from 0.5:1 to 2:1. While the Ir(I) complexes were not characterized directly, their existence is based on the unambiguous structural assignments of the corresponding H_2 oxidative addition products through parahydrogen induced polarization. The chemical shifts and J_{Sn-H} coupling constants of the PHIP-enhanced resonances have been described previously and are summarized in Table 1. Figures 1−3 illustrate the appropriate resonances. In all cases except for **8** which is not seen with polarization, the iridium(III) dihydride species are presumed to form by the cis concerted addition of eq 1 and therefore report faithfully the geometry of the respective Ir(I) isomers from which they are produced.

When excess tin dibromide is present, the insertion equilibrium is shifted to right, and at 3:1 or greater ratios of $SnBr_2$/**1**, only bis(tribromostannyl) complexes are present, as indicated by PHIP spectra of their dihydrogen oxidative addition products. The exchange of tin tribromide between Ir(I) species in systems without added halide proceeds by either $SnBr_3^-$ dissociation and recoordination or by elimination of $SnBr_2$ and subsequent reinsertion. Coexistence of all four Ir(I) tribromostannyl complexes (i.e., **2-cis**, **2-trans**, **3-cis**, and **3-trans**) indicates comparable thermodynamic stability. The rate of exchange of bromide and tribromostannyl ligands in the Ir(I) complexes is uncertain, but for the Ir(III) dihydrides, the exchange is slow as evidenced by the observation of J_{Sn-H} couplings and the absence of any line-broadening arising from exchange.

Formation of Ir(III) Tribromostannyl Dihydrides. Figure 4 shows schematically how the different mono- and bis(tribomostannyl) dihydride products form by oxidative addition of H_2 to the respective isomers of **2** and **3**. On the basis of polarization studies, complex **5** is the kinetic product of H_2 oxidative addition to **2** as the cis isomer, while the bis(tribromostannyl) complexes **3** exhibit greatly reduced reactivity with H_2. Of all of the dihydride complexes identified, only the mono(tribromostannyl) species **8** and the bis(tribromostannyl) complex **11** are seen under normal hydrogen. In these spectra, the resonance for **11** exhibits observable tin satellites whereas the resonance for **8** is weaker with no definite satellite signals seen. The absence of polarization for these complexes, because of hydride equivalence in the absence of other spin-active nuclei, makes direct comparison of their concentrations relative to those of the PHIP-enhanced dihydrides not meaningful, but they appear to be far more stable. While complex **11** forms only at temperatures greater than 45 °C, its intensity increases with time, showing it to be the thermodynamic product of the bis(tribromostannyl) complexes regardless of whether its formation is by direct H_2 oxidative addition or by rearrangement from one of the other dihydride products. This contrasts with the behavior of the kinetic product **5**, which forms at 20 °C and whose polarization decays rapidly as para-enriched hydrogen in solution returns to a normal hydrogen distribution by oxidative addition and reductive elimination. Removal of the sample from the probe, shaking to restore para-enriched hydrogen in solution and reinsertion into the spectrometer restores the strong polarization for **5**.

Intensity of PHIP Resonances and Relative Rates of Formation of Ir(III) Dihydrides. The intensity of PHIP signals is determined by a number of factors including the rate of reaction generating product with non-Boltzmann spin populations, the hydride relaxation times, the depletion of

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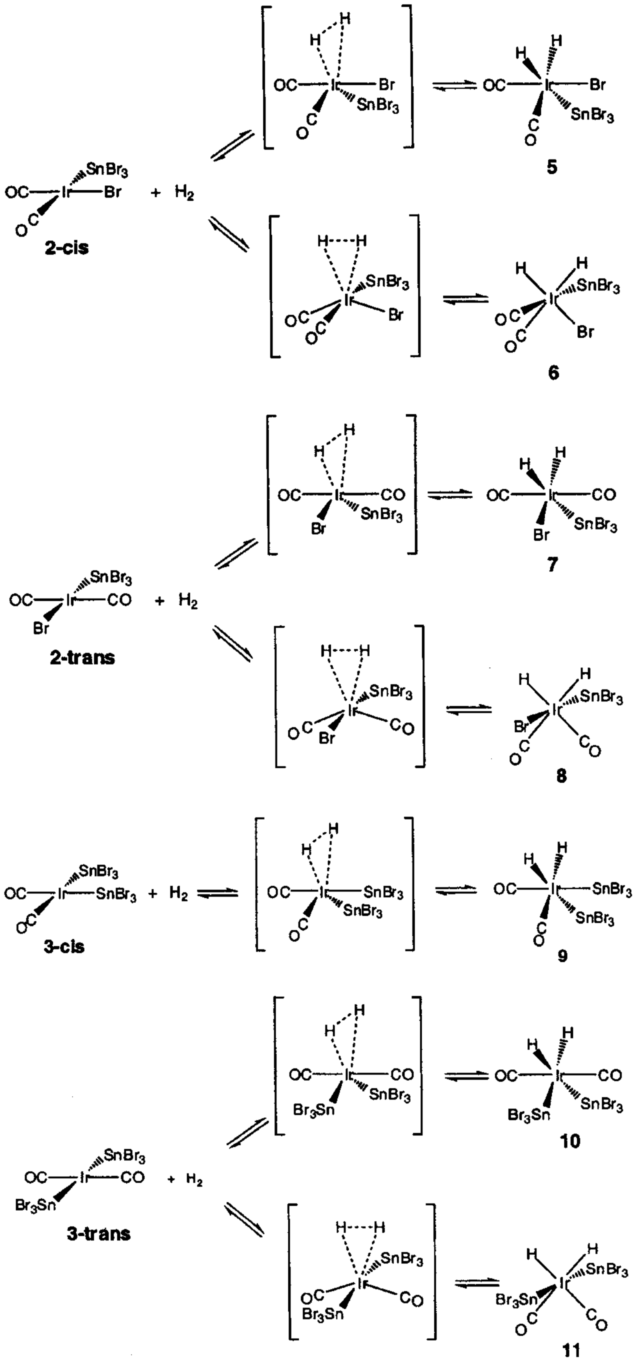

Figure 4. Different stereochemical pathways for concerted cis addition of H_2 to Ir(I) mono- and bis(tribromostannyl) complexes **2** and **3**.

parahydrogen enrichment in solution by hydrogen cycling (oxidative addition−reductive elimination), and the replenishment of para-enriched H_2 in solution by gas−solution mixing. Aside from the last of these which is very slow, the other factors are system dependent and variable. It is therefore not quantitatively correct to equate relative magnitude of polarization with relative rate of dihydride formation in the absence of other measurements. However, qualitative assessments appear to be valid.

Of the bromo tribromostannyl dihydrides, **6** and **7** form less easily than the kinetic isomer **5**, although their polarized intensities increase relative to that of **5** at elevated temperatures. In these measurements, the polarization for **7** is greater than that for **6**. Both of these dihydrides, however, are not observable under normal hydrogen unlike PHIP-silent **8** which appears to be the most stable. From these results, we suggest a relative order for H_2 addition along the particular axis of the Ir(I) complex as $OC-Ir-SnBr_3 > Br-Ir-SnBr_3 > OC-Ir-Br > OC-Ir-CO$.

For the bis(tribromostannyl) dihydrides, complex **11** appears to be most stable, but its formation is slowest, whereas dihydride **9** has the strongest polarization, suggesting that its formation is most rapid. However, the symmetry of isomer **10** precludes direct comparison with **9** because polarization is only seen for the former species in the $^{117,119}Sn$ satellites. For **9**, the axis of addition is $OC-Ir-SnBr_3$ whereas for **10** the axis of addition is $Br_3Sn-Ir-SnBr_3$. For the thermodynamic product **11**, the axis of addition is OC−Ir−CO. The kinetic order for addition thus parallels that proposed for the bromo tribromostannyl complexes except that the latter do not possess a $Br_3Sn-Ir-SnBr_3$ axis for comparison.

Comments on H_2 Oxidative Addition to Ir(I) Carbonyl Anions. Unlike the reactivity of neutral Ir(I) complexes for H_2 oxidative addition, anionic systems are considerably less reactive despite the fact that the reaction involves formal metal oxidation. Theoretical analyses[9,54−56] of H_2 oxidative addition indicate three key interactions as determining the kinetic barrier for the addition process, these being (a) σ-donation from the filled $\sigma^b(H_2)$ orbital into the vacant M p_z orbital; (b) π-back-bonding from a filled M d_π orbital into the $\sigma^*(H_2)$ orbital; and (c) interaction between the filled σ^b-(H_2) orbital and the filled M d_{z^2} function. The first two correspond to the usual synergic interaction for oxidative addition, while (c) represents a repulsive $4e^-$ interaction that is viewed as the main determinant in establishing the kinetic barrier for the reaction. For anionic complexes, the kinetic barrier for H_2 oxidative addition increases as the filled M d_{z^2} function becomes more spatially extended.

From the results of the present study and those reported by Duckett for the $IrI_2(CO)_2^- + H_2$ reaction system,[47] it is evident that oxidative addition of H_2 to Ir(I) carbonyl anions does indeed occur. It thus appears that this reaction is limited thermodynamically rather than kinetically, as suggested by the theoretical analyses. The activating role of $SnBr_2$ to H_2 oxidative addition is also clear from experiments in which only half an equivalent of $SnBr_2$ is added to $IrBr_2(CO)_2^-$ leading to much stronger polarization in the formation of *cis,cis*-$IrH_2Br(SnBr_3)(CO)_2^-$ (**5**) than in the formation of *cis,cis,cis*-$IrH_2Br_2(CO)_2^-$ (**4**) in the same sample. Qualitatively, the bromo tribromostannyl complex **2-cis** is kinetically most active, and the preferred orientation of H_2 along the $OC-Ir-SnBr_3$ axis suggests the benefits of both $SnBr_3^-$ σ-donation for back-bonding into the H_2 σ^* orbital and CO and $SnBr_3^-$ π-acidity to reduce the repulsive interaction involving the filled $\sigma^b(H_2)$ and filled M d_{z^2} orbitals.

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Conclusions

The present study reveals the power of PHIP in observing and identifying dihydride complexes generated in situ by H_2 oxidative addition. While H_2 oxidative addition to Ir(I) carbonyl anions is not thermodynamically favorable under 1−3 atm of hydrogen, the present results show that the reaction does proceed reversibly at temperatures up to 75 °C for the $[IrBr_n(SnBr_3)_{2-n}(CO)_2]^-$, $n = 0$, 1 set of complexes. The resultant PHIP spectra make possible the unequivocal assignment of the structures of six different dihydride complexes, all of which form by concerted cis addition to the respective Ir(I) anionic precursors. It is seen that $SnBr_2$ strongly enhances the reactivity of Ir(I) dicarbonyl anions to reaction with H_2 through the formation of tribromostannyl complexes. Through the signal enhancements of PHIP and the chemical shifts and $^1H-^{117,119}Sn$ coupling constants of the resultant hydride resonances, the stereoselectivity of H_2 oxidative addition has been established. The kinetic isomer for H_2 oxidative addition to the mixed *cis*-bromo-tribromostannyl complex $IrBr(SnBr_3)_{2-n}(CO)_2^-$ (**2-cis**) is **5** while that for addition to the *trans*-bromo-tribromostannyl isomer **2-trans** is **7**. With $SnBr_2/IrBr_2(CO)_2^-$ concentration ratios of 3 or greater, the relative activity of Ir(I) carbonyl anions to H_2 oxidative addition as seen through PHIP diminishes, while, at these relatively higher $SnBr_2$ concentrations, the thermodynamic isomer for the system is identified as **11**. This isomer is seen by conventional ^1H NMR spectroscopy. The use of PHIP in the present study is qualitative in terms of accurate estimates of the relative concentrations of dihydride species, but it is definitive in the assignment of dihydride structures. The most stable dihydrides, two of which can be seen in conventional ^1H NMR spectra, contain trans H−Ir−CO linkages and are apparently stabilized by complementary interactions of hydride and carbonyl ligands.

Experimental Section

All operations were performed under a nitrogen atmosphere using either a Vacuum Atmospheres glovebox or a vacuum line. Acetone (Cambridge Isotope Laboratories, Inc.) was degassed before use. Para-enriched hydrogen corresponding to an approximately 1:1 ratio of parahydrogen and orthohydrogen was generated by cooling hydrogen (Air Products, Inc.) to 77 K at 1 atm pressure in the presence of silica impregnated with paramagnetic salts. NMR spectra were recorded on a Bruker Avance 400 spectrometer with variable temperature controller. The $^1H-^1H$ COSY correlation was taken with 32 pulses acquisition in F2 and 32 points in the F1 time domain. The standard COSY sequence was modified with the first pulse set to 45° and the second to 90° as described previously.[22]

Anhydrous tin dibromide was prepared by the reaction of metallic tin with aqueous HBr and drying of the product in a vacuum. Tetrabutylammonium dibromodicarbonyliridate, $(Bu_4N)[IrBr_2(CO)_2]$, was prepared as previously described.[57] The NMR samples were prepared by condensing of 0.7 mL of acetone-d_6 into an NMR tube containing solid $(Bu_4N)[IrBr_2(CO)_2]$ and tin dibromide and fitted with a J. Young valve. The tubes were allowed to stand overnight, after which the samples were frozen, evacuated, and placed under 1 atm para-enriched hydrogen at 77 K, corresponding to ∼3 atm pressure at 298 K. The NMR spectra were taken after thawing and vigorous shaking of the tubes and warming them inside the probehead at least for 1.5 min to the desired temperature. A 45° pulse was used for all spectra, some of which were obtained from single pulse experiments and some from 16 or 32 scans.

Labeling Experiments. A solution of $(Bu_4N)[IrBr_2(CO)_2]$ (6.5 mg, 10 μM) and $SnBr_2$ (8.4 mg, 30 μM) in 0.7 mL of acetone-d_6 was prepared. Approximately 0.1 mL of the solution was then transferred in a glovebox to another NMR tube, and 0.6 mL of acetone-d_6 was added. Both solutions were degassed on a vacuum line, and ^{13}CO (Cambridge Isotope Laboratories, Inc., 99% labeled) was then introduced. The solutions were allowed to stand overnight with occasional shaking. The gaseous ^{13}CO atmosphere was then removed, and para-enriched hydrogen was introduced as described for the rest of the samples. Examination of the PHIP spectra showed that the solution having the higher concentration of iridium species (14 mM) contained a mixture of mono- and unlabeled $IrBr_2(CO)_2^-$, while the more dilute solution (2 mM) consisted mainly of bis-labeled $IrBr_2(CO)_2^-$ together with approximately 30% of mono-labeled species.

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