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Registry No. **4**, 114762-89-9; **4**-d_3, 114762-95-7; **5**, 114762-90-2; **6**, 114762-91-3; **7**, 114762-92-4; **7**-d_3, 114762-96-8; **8**, 114762-93-5; **9**, 114762-94-6; 2,6-$(Me_2NCH_2)_2C_6H_3Br$, 66479-06-9; $[IrCl(COD)]_2$, 12112-67-3; 1-Me-2-Br-3-$(Me_2NCH_2)C_6H_3$, 114739-32-1; $Li_4[C_6H_4(CH_2NMe_2)\text{-}2]_4$, 56174-66-4; 2-Br-1,3,5-$(Me_2NCH_2)_3C_6H_2$, 114739-29-6; 2-bromo-1,3-dimethylbenzene, 576-22-7; 2-bromo-1,3-dimethylbenzene-d_3, 114739-30-9; 2-bromo-1,3-bis((dimethylamino)methyl)benzene-d_3, 114739-31-0.

Supplementary Material Available: Lists of hydrogen atom positions and thermal parameters and complete lists of bond distances and angles (4 pages); a listing of the F_o and F_c values (25 pages). Ordering information is given on any current masthead page.

Formation of Octahedral Iridium(III) Dihydrides from the Reaction of Ortho-Chelated Aryliridium(I) Compounds with Dihydrogen

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The reaction of $Ir^I[C_6H_2(CH_2NMe_2)\text{-}2\text{-}R^1\text{-}4\text{-}R^2\text{-}6](COD)$ (COD = cycloocta-1,5-diene) with dihydrogen in CD_2Cl_2 was monitored by ^1H NMR. At −20 °C quantitative formation of the novel dihydride complexes $Ir^{III}H_2[C_6H_2(CH_2NMe_2)\text{-}2\text{-}R^1\text{-}4\text{-}R^2\text{-}6](COD)$ [R^1 = H, R^2 = CH_2NMe_2 (**10**), Me (**11**); R^2 = H, R^1 = H (**12**), Me (**13**), CH_2NMe_2 (**14**); $R^1 = R^2 = CH_2NMe_2$ (**15**)] occurs. Further reactions, the type of which depends on the bulkiness of the R^1 and R^2 groups, occur when these solutions are warmed to 0 °C. Complexes **12**–**14** (R^2 = H) lose H_2 to re-form $Ir^I[C_6H_3(CH_2NMe_2)\text{-}2\text{-}R^1\text{-}4](COD)$. In contrast, complexes **10**, **11**, and **15** (R^2 = alkyl) react further by means of C(aryl)–H reductive elimination. For complex **15** ($R^1 = CH_2NMe_2$) this results in quantitative formation of 1,3,5-$(Me_2NCH_2)_3C_6H_3$ and "IrH(COD)". In $Ir^{III}H_2[C_6H_3(CH_2NMe_2)\text{-}2\text{-}R\text{-}6](COD)$ [R = alkyl (**10** and **11**)], C(aryl)–H reductive elimination is followed by re-addition of another C(aryl)–H bond, which upon subsequent reductive elimination of H_2, yields the *rearranged* iridium(I) complexes $Ir^I[C_6H_3(CH_2NMe_2)\text{-}2\text{-}R\text{-}4](COD)$. Since the rearrangement of $Ir^I[C_6H_3(CH_2NMe_2)\text{-}2\text{-}R\text{-}6](COD)$ to $Ir^I[C_6H_3(CH_2NMe_2)\text{-}2\text{-}R\text{-}4](COD)$ can also be induced thermally at 60 °C, it is therefore being catalyzed by dihydrogen at 0 °C. None of these reactions with dihydrogen is attended by hydrogenation of the COD ligand.

Introduction

The oxidative addition of dihydrogen to metal d^8 complexes is a key step in homogeneous hydrogenation and hydroformylation catalysis.[1] Since the discovery of the first stable metal dihydrido olefin complexes in 1976 by Crabtree et al.,[2] several papers have emerged on the observation of other species of this type.[3] These species, as well as recently isolated *cis*-alkyl/aryl/acyl hydride rhodium and iridium complexes,[4] can be regarded as intermediates in the homogeneous catalytic hydrogenation of olefins.

In previous papers we reported the syntheses of $M^I[C_6H_3(CH_2NMe_2)\text{-}2\text{-}R\text{-}6](COD)$ [M = Rh, R = CH_2NMe_2 (**1**), Me (**2**), H (**3**);[5] M = Ir, R = CH_2NMe_2 (**4**), Me (**5**), H (**6**)] and $Ir^I[C_6H_2(CH_2NMe_2)_3\text{-}2,4,6](COD)$ (**9**);[6] see Figure 1. We also reported that compounds **4** and **5**, which suffer from internal steric crowding between the 6-substituted alkyl group and the adjacent COD double bond, isomerize quantitatively in an unusual way to $Ir^I[C_6H_3(CH_2NMe_2)\text{-}2\text{-}R\text{-}4](COD)$ [R = CH_2NMe_2 (**7**) and Me (**8**), respectively]. The mechanism of this conversion involves the successive intramolecular breaking and making of several C–H bonds (see Scheme I). Some of the postulated intermediates in this conversion involve iridium(III) hydride species yet, despite the cis arrangement of the metal hydride and one of the double bonds of COD, no hydrogenation of COD was observed. In view of this it was anticipated that the reaction of molecular hydrogen with the iridium(I) complexes **4**–**9** might lead to isolable iridium(III) dihydride species. This paper contains the results

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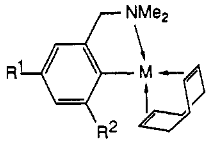


R^1	R^2	M = Rh	M = Ir
H	CH_2NMe_2	1	4
H	Me	2	5
H	H	3	6
CH_2NMe_2	H		7
Me	H		8
CH_2NMe_2	CH_2NMe_2		9

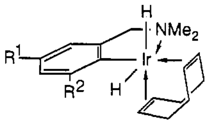
Figure 1. Solid-state structures of $M^I[C_6H_2(CH_2NMe_2)$-2-R^1-4-R^2-6](COD) (1–9).

of these investigations that have led to the identification of dihydride complexes that also bear olefin and aryl functions around the iridium center.

Experimental Section

General Data. All manipulations were conducted under an atmosphere of dry nitrogen. The compounds $Ir[C_6H_3(CH_2NMe_2)_2$-2,6](COD) (4), $Ir[C_6H_3(CH_2NMe_2)$-2-Me-6](COD) (5), $Ir[C_6H_4(CH_2NMe_2)$-2](COD) (6), $Ir[C_6H_3(CH_2NMe_2)_2$-2,4](COD) (7), $Ir[C_6H_3(CH_2NMe_2)$-2-Me-4](COD) (8), and $Ir[C_6H_2(CH_2NMe_2)_3$-2,4,6](COD) (9) were synthesized according to ref 6.

Reaction of the Iridium(I) Complexes (4–9) with H_2. Formation of Dihydride Species and NMR Measurements. In a typical experiment a red solution of ca. 0.15 mmol of one of the iridium complexes, 4–9, in 1.5 mL of dry CD_2Cl_2 was cooled to −20 (±5) °C. When hydrogen was bubbled through this solution for ca. 1 min, a clear yellow solution resulted. At this temperature, 0.5 mL of the reaction mixture, containing the iridium(III) dihydride complex, was transferred to a precooled 5-mm NMR tube. Subsequent ^1H NMR spectra were recorded first at −20 °C and then with increasing temperature at intervals of 10° up to +20 °C on a Bruker WM250 spectrometer.



R^1	R^2	Starting Iridium(I) complex	Iridium(III) dihydride complex
H	CH_2NMe_2	4	10
H	Me	5	11
H	H	6	12
CH_2NMe_2	H	7	13
Me	H	8	14
CH_2NMe_2	CH_2NMe_2	9	15

Figure 2. Structures of $Ir^{III}H_2[C_6H_2(CH_2NMe_2)$-2-$R^1$-4-$R^2$-6](COD) (10–15) in solution at −20 °C.

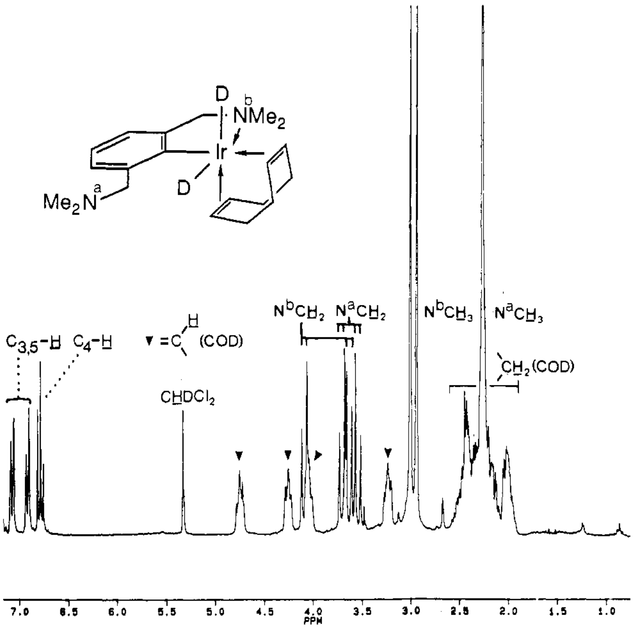


Figure 3. ^1H NMR spectrum of $Ir^{III}D_2[C_6H_3(CH_2NMe_2)_2$-2,6](COD) (10-$d_2$) in CD_2Cl_2 at −20 °C.

Results and Discussion

Formation and Characterization of $Ir^{III}H_2[C_6H_2(CH_2NMe_2)$-2-$R^1$-4-$R^2$-6](COD) (10–15). The orange-red complexes $Ir^I[C_6H_2(CH_2NMe_2)$-2-R^1-4-R^2-6](COD) (4–9) have square-planar configurations in the solid state, with a C,N-coordinated aryl ligand and a bidentate COD ligand (Figure 1).[6] Bubbling dihydrogen through solutions of these complexes in CD_2Cl_2 at −20 (±5) °C results in rapid formation of a yellow solution containing the iridium(III) dihydride species $Ir^{III}H_2[C_6H_2(CH_2NMe_2)$-2-$R^1$-4-$R^2$-6](COD) (10–15) (Figure 2). The oxidative addition reaction proceeded very cleanly in this narrow temperature range, and ^1H NMR measurements at −20 °C of these clear solutions showed the iridium(III) dihydrides to be the only species present. As complexes 10–15 were found to be unstable above 0 °C in solution, identification was restricted to in situ ^1H NMR spectroscopy and no attempts were made to isolate solid products.

The iridium(III) dihydride complexes 10–15 can be readily characterized by their distinctive ^1H NMR spectra (Table I and Figure 3). There are two hydride resonances with equal intensity at ca. −9 and −17 ppm, which are singlets within the resolution of the NMR measurements (0.5 Hz). The four olefinic protons of COD appear as four separate signals, indicative of the complete absence of

Scheme I. Postulated Mechanism for the Conversion of $Ir^I[C_6H_3(CH_2NMe_2)$-2-R-6](COD) [R = CH_2NMe_2 (4), Me (5)] to $Ir^I[C_6H_3(CH_2NMe_2)$-2-R-4](COD) [R = CH_2NMe_2 (7), Me (8)][6]

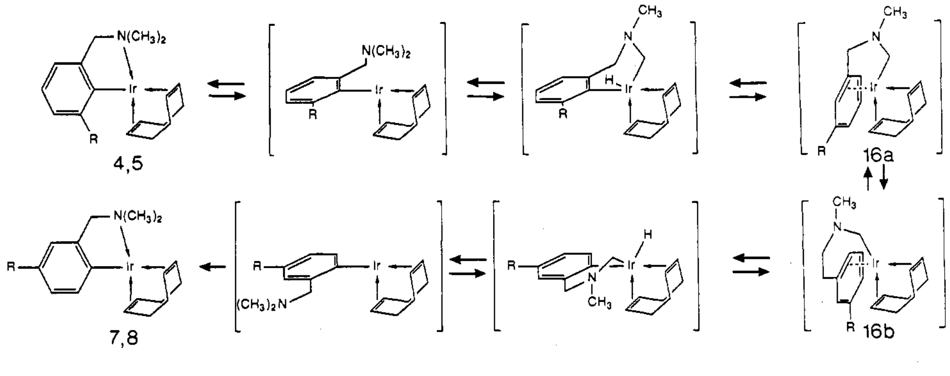


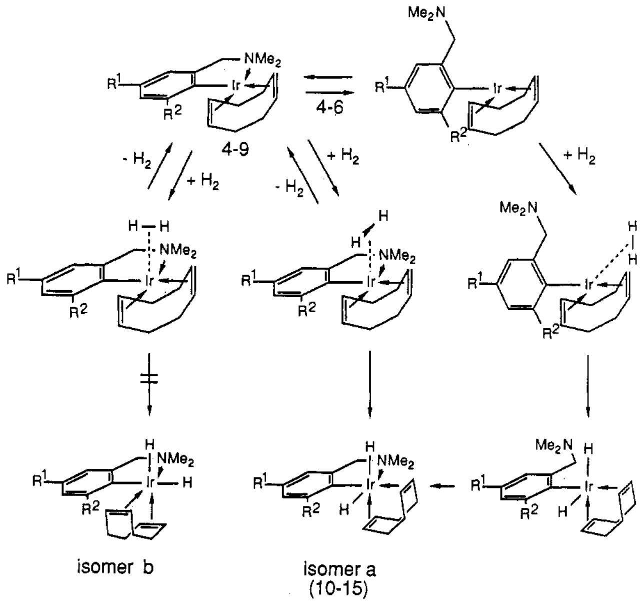
Table I. ^{1}H NMR Data of $IrH_2[C_6H_2(CH_2NMe_2)\text{-}2\text{-}R^1\text{-}4\text{-}R^2\text{-}6](COD)$[a]

			2-CH_2NMe_2 group				
compd	R^1	R^2	CH_2	$N(CH_3)_2$	other aromatic protons and substituents[b]	$=CH(COD)$[c]	IrH
10	H	CH_2NMe_2	3.63 (d), 4.08 (d)	2.94 (s), 3.00 (s)	$H_{3,5}$, 6.91 (d), 7.07 (d); H_4, 6.78 (t); R^2, CH_2, 3.53 (d), 3.70 (d), CH_3, 2.26 (s)	3.25, 4.03, 4.25, 4.74	−9.37, −16.41
11	H	Me	3.63 (d), 4.10 (d)	2.97 (s), 3.01 (s)	$H_{3,5}$, 6.89 (d), 6.86 (d); H_4; 6.70 (t); R^2, CH_3, 2.50 (s)	3.23, 4.07, 4.21, 4.77	−9.12, −16.44
12	H	H	3.68 (d), 3.84 (d)	2.68 (s), 3.12 (s)	H_3, 6.99 (d); $H_{4,5}$, 6.75 (t), 6.81 (t); H_6, 7.49 (d)	2.83, 4.09, 4.61, 4.74	−9.16, −17.88
13	CH_2NMe_2	H	3.66 (d), 3.83 (d)	2.67 (s), 3.11 (s)	H_3, 6.94 (s); H_5, 6.71 (d); H_6, 7.40 (d); R^1, CH_2, 3.19 (s), CH_3, 2.11 (s)	2.82, 4.08, 4.61, 4.72	−9.17, −17.91
14	Me	H	3.65 (d), 3.83 (d)	2.66 (s), 3.13 (s)	H_3, 6.87 (s); H_5, 6.69 (d); H_6, 7.38 (d); R^1, CH_3, 2.51 (s)	2.83, 4.09, 4.62, 4.75	−9.13, −17.86
15	CH_2NMe_2	CH_2NMe_2	3.62 (d), 4.04 (d)	2.94 (s), 2.96 (s)	$H_{3,5}$, 6.97 (s), 6.84 (s); R^1, CH_2, 3.20 (s); CH_3, 2.11 (s); R^2, CH_2, 3.53 (d), 3.70 (d), CH_3, 2.11 (s)	3.23, 4.03, 4.25, 4.74	−9.43, −16.47

[a] Measured in CD_2Cl_2 at −20 °C and 250 MHz. Chemical shifts (δ) relative to external TMS. [b] For adjacent aryl protons, $^3J(H\text{–}H) = 7$ Hz; for CH_2 AB doublets, $^2J(H\text{–}H) = 13$ Hz. [c] Broad resonance.

symmetry in these complexes. Finally, there is a single aryl ligand, which for all these complexes shows diastereotopic CH_2 protons and NMe_2 methyls in (one of) the CH_2NMe_2 group(s). This chirality of the N atom can only arise if this CH_2NMe_2 group is coordinated to the iridium center, and therefore the aryl ligand in complexes **10–15** is always bidentate C,N-coordinated. Together with the two hydrides and the two coordinated double bonds of COD, this adds up to a six-coordinate iridium(III) complex, which almost certainly has a monomeric octahedral structure. Since the ^{1}H NMR data of the hydrides and olefinic protons of COD in **10–15** are all fairly similar, these complexes are believed to be isostructural.

Scheme II. Possible Pathways for the Cis Addition of Dihydrogen to $Ir^I[C_6H_2(CH_2NMe_2)\text{-}2\text{-}R^1\text{-}4\text{-}R^2\text{-}6](COD)$ (4–9) Leading to the Formation of $Ir^{III}H_2[C_6H_2(CH_2NMe_2)\text{-}2\text{-}R^1\text{-}4\text{-}R^2\text{-}6](COD)$ (10–15)



A symmetrical structure in which the hydride atoms are in trans positions can be ruled out immediately on the basis of the above NMR data. There remain two other possible octahedral structures for these iridium(III) dihydrides in which the two hydrides are both in cis positions (isomers a and b in Scheme II). Despite the fact that the hydride atoms must be cis positioned, no mutual coupling was observed, but such couplings are usually very small (<2 Hz).[3,7-9] Spectroscopically, the two postulated structures a and b can be discriminated on the basis of the ^{1}H chemical shifts of the hydride atoms. It is known that the chemical shifts of iridium hydride resonances keep a reliable track of the electronegativity of the opposing trans group.[10] Thus, the ^{1}H NMR resonances of trans-C (either double bond or aryl/alkyl) hydrides are expected at ca. −11 (±2) ppm and those of trans-N hydrides at ca. −18 (±2) ppm. Accordingly, the hydride that appears at −17 ppm in complexes **10–15** should be trans to a nitrogen atom, which means that these complexes have structures designated as isomer a in Scheme II. Additionally, other facts point to a as being the most likely structure: (i) if complexes **10, 11,** and **15** had structure b, there would be severe steric hindrance between the 6-substituted R^2 group and the trans-N olefinic group of COD; (ii) the resonances of one of the hydrides appear in the extremely narrow range of −16.44 (±0.03) ppm for the three complexes **10, 11,** and **15** and of −17.89 (±0.03) ppm for the other three complexes **12–14**. This clear difference can only be readily explained by the influence of the adjacent R^2 group in structure a, which is a proton in complexes **12–14** and an alkyl group in complexes **10, 11,** and **15**. Such behavior would not expected for the trans-C(aryl) hydride of structure b because here it has the same spatial environment in all six iridium(III) complexes, **10–15**. Evidently, the introduction of a 6-position alkyl group into the iridium(III) dihydride complexes **10, 11,** and **15** causes a deshielding of the trans-N hydride atom and a consequent downfield shift of 1.45 ppm. Finally, it is worth noting that in accordance with structure a, the other hydride (which is trans to a double bond of COD) resides in a position that is far away from the R^2 group, which explains why its ^{1}H chemical shift of −9.28 (±0.15) ppm does not differ much within the six iridium(III) dihydrides.

Complexes **10–15** are rare examples of iridium(III) species having olefin, aryl, and hydride functions together around the same metal center. To our knowledge, the only other complex having this feature is dinuclear PhH(COD)Ir(μ-$C_{12}H_8$)Ir(COD).[11] It is further noted that the new hydrides **10–15** are structurally related to the cationic

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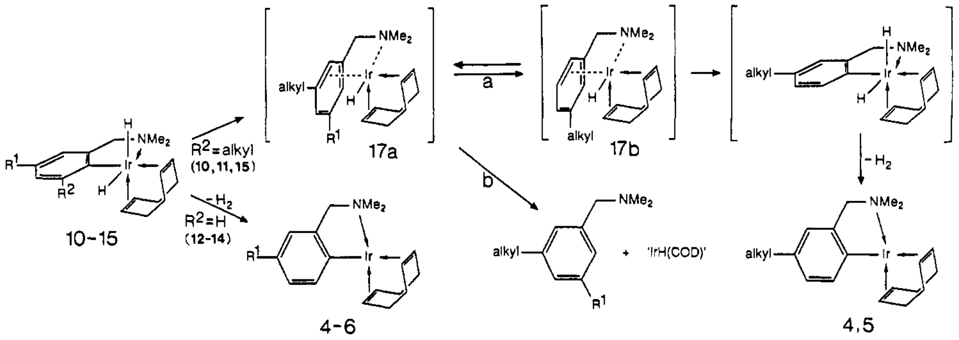
Scheme III. Thermally Induced Reactions of $Ir^{III}H_2[C_6H_2(CH_2NMe_2)$-2-$R^1$-4-$R^2$-6](COD) (10–15) upon Warming in Solution from −20 to 0 °C



Route	a	b
R^1 = H (10,11)	70%	30%
10 in the presence of 2 PPh_3	0%	100%
R^1 = alkyl = CH_2NMe_2 (15)	0%	100%

complexes $[IrH_2(COD)L_2]^+$, which currently are the most active catalysts known for the homogeneous hydrogenation of olefins.[2]

Mechanism of Dihydrogen Addition to $Ir^I[C_6H_2(CH_2NMe_2)$-2-R^1-4-R^2-6](COD) (4–9). Knowing the geometry of the new iridium(III) dihydrides 10–15, it is now possible to discuss the available pathways for their formation from the iridium(I) precursors 4–9 (summarized in Scheme II). As mentioned earlier, the iridium(I) complexes 4 and 5, as well as 9, suffer from steric crowding of the 6-position aryl R^2 group and an adjacent double bond of COD. In solution these complexes relieve their strain by a reversible dissociation of the Ir–N bond, followed by rotation of the aryl ligand out of the coordination plane, thereby creating a T-shaped 14-electron intermediate (see Scheme I, upper left, or Scheme II, upper part). It has been shown that this intermediate is the actual species that reacts intramolecularly with an NMe C–H bond to initiate the unique irreversible rearrangement depicted in Scheme I.[6] However, irrespective of this fluxionality, compounds **4**, **5**, and **9** as well as the nonfluxional compounds **6–8** react with dihydrogen to afford the isostructural *cis*-dihydride species **10–15**. This means that attack of dihydrogen on the T-shaped three-coordinate species as well as on the square-planar four-coordinate species yields the same type of product.

A concerted cis addition of H_2 to the square-planar arrangement of the iridium(I) complexes **4–9** can take place along either the N–Ir–olefin or the C(aryl)–Ir–olefin′ axis, affording the octahedral iridium(III) dihydride structures a and b, respectively (see Scheme II). In the present case, isomer b is unlikely on steric grounds, and although this type of dihydrogen addition is often under kinetic control,[3b,8] here it must be guided by thermodynamic factors.

For complexes **4**, **5**, and **9** dihydrogen can also add to the T-shaped three-coordinate conformation. Oxidative addition to such a species will normally be directed (on steric grounds) such that a diatomic substrate approaches the metal center oriented perpendicular to the coordination plane with its midpoint in this plane to afford a five-coordinate complex (Scheme II, right).[12] In accordance with the observed product formation, the two hydrides then remain mutually cis, since upon subsequent intramolecular coordination of the tertiary amine group the octahedral cis-dihydride complexes **10**, **11**, and **15** are generated. However, without further information it is impossible to say by which of the two mechanisms outlined here the fluxional iridium(I) complexes 4, 5, and 9 react with dihydrogen.

Reactions of $Ir^I[C_6H_2(CH_2NMe_2)$-2-R^1-4-R^2-6](COD) (4–9) with Dihydrogen at Other Temperatures. In contrast to the behavior of the iridium(I) complexes 4–9 with dihydrogen at −20 °C, at temperatures below ca. −40 °C no measurable reaction was observed, despite the presumed enhanced thermodynamic preference for dihydride formation. This is in accord with theoretical calculations by Saillard and Hoffmann.[13] They state that side-on dihydrogen additions to planar d^8-ML_4 complexes proceed better if two trans ligands can bend toward each other (in the *yz* plane). This destabilizes the d_{yz} orbital, which can than provide an improved overlap with the dihydrogen σ^* orbital. This situation can only be reached if these complexes exhibit sufficient thermal motion. This temperature-dependent behavior of the iridium(I) complexes 4–9 toward dihydrogen points to the conclusion that a slight bending in these square-planar metal d^8 complexes is indeed required to induce a side-on addition of dihydrogen.

The reaction of the iridium(I) complexes 4–9 with dihydrogen, when carried out at room temperature, led to gradual decomposition and formation of 1-(Me_2NCH_2)-3-R^1-5-R^2-C_6H_3, cyclooctane, and probably metallic iridium. The kinetic barriers are now low enough at this temperature for hydrogenation of the double bonds of COD.

Finally in this section, it is worth noting that the analogous rhodium(I) complexes 1–3 also exhibit a temperature-dependent behavior toward molecular hydrogen. However, they differ from the iridium(I) complexes in that there was no intermediate temperature range in which rhodium(III) dihydride species could be detected.[5]

Thermally Induced Reactions of $Ir^{III}H_2[C_6H_2(CH_2NMe_2)$-2-$R^1$-4-$R^2$-6](COD) (10–15). Solutions of the iridium(III) dihydride complexes 10–15, prepared from 4–9 in situ in CD_2Cl_2 at −20 °C, undergo various reactions on warming to +20 °C. These reactions were monitored by ^1H NMR, and in all cases the resonances assigned to $Ir^{III}H_2[C_6H_2(CH_2NMe_2)$-2-$R^1$-4-$R^2$-6](COD) disappear above 0 °C. The types of reaction that take place, summarized in Scheme III, are found to depend primarily on the bulkiness of the R^2 group of the aryl ligand.

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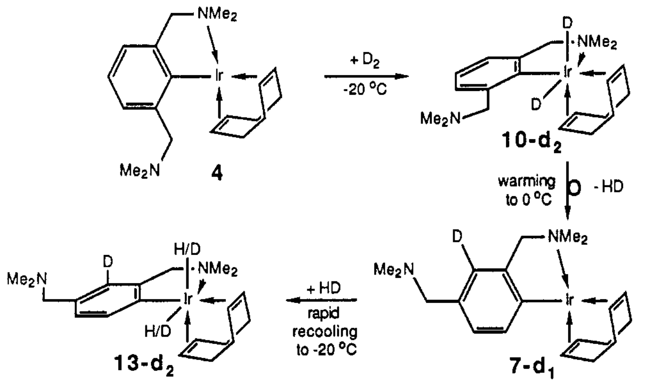

Figure 4. Reaction of Ir^{I}[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6](COD) (4) with D$_2$.

Complexes 12–14, which all have a proton at the 6-position of the aryl ligand (R^2 = H), lose dihydrogen quantitatively, re-forming their starting iridium(I) complexes 6–8, respectively. The reaction of 6–8 with dihydrogen to form the dihydrides 12–14 is therefore reversible.

However, complexes 10, 11, and 15, which all have an alkyl group as R^2, do not give back their respective iridium(I) precursors on warming. Instead of Ir^{I}[C$_6$H$_3$(CH$_2$NMe$_2$)-2-R-6](COD) [R = CH$_2$NMe$_2$ (4), Me (5)], the respective dihydrides 10 and 11 yield mainly the rearranged isomers Ir^{I}[C$_6$H$_3$(CH$_2$NMe$_2$)-2-R-4](COD) (7 and 8) (70%), accompanied by some decomposition to 1-(Me$_2$NCH$_2$)-3-R-C$_6$H$_4$ and "IrH(COD)" (30%).[14] If a solution of Ir^{III}H$_2$[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6](COD) (10) (which itself does not react with PPh$_3$) is warmed up in the presence of 2 equiv of PPh$_3$, a 1:1 mixture of 1,3-(Me$_2$NCH$_2$)$_2$C$_6$H$_4$ and the known[17] complex IrH(COD)(PPh$_3$)$_2$ is obtained, so corroborating the formation of a "IrH(COD)" moiety during the reaction.[14] Complex 15 reacts on warming to afford only 1,3,5-(Me$_2$NCH$_2$)$_3$C$_6$H$_3$ as the organic product.

In contrast to the H–H elimination of the dihydride complexes 12–14, the nature of the reaction products of the iridium(III) dihydrides 10, 11, and 15 points to C(aryl)–H reductive elimination pathways. The 6-position alkyl groups in these latter complexes appear to exert a repulsive force on the neighboring hydride atom such that C(aryl)–H reductive elimination becomes more favorable than dihydrogen elimination.

For 10 and 11, the formation of the iridium(I) complexes 7 and 8 suggests a rearrangement process (see Scheme III) very similar to that found for the thermal conversion of complexes 4 and 5 to 7 and 8 at 60 °C (see Scheme I). This latter process has been shown to be triggered by a C–H addition of a MeN group to the iridium(I) center.[6] In the former process, addition of H–H initiates the intramolecular rearrangement, which now proceeds at a much lower temperature (0 °C), and therefore dihydrogen is actually acting as a catalyst.

The mechanism of the dihydrogen catalyzed 4/7 and 5/8 rearrangement was examined by following the reaction of Ir^{I}[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6](COD) (4) with dideuterium (see Figure 4). At −20 °C this yields, as anticipated, Ir^{III}D$_2$[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6](COD) (10-d_2). When the mixture was warmed to 0 °C, Ir[C$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,4-D-3](COD) (7-d_1) was formed exclusively. Although the concomitant formation of HD in this briefly warmed solution was not demonstrated directly, rapid recooling of the reaction mixture to −20 °C resulted in the formation of a species formulated as Ir^{III}HD[C$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,4-D-3](COD) (13-d_2). Its ^{1}H NMR spectrum has hydride signals at −9.2 and −17.9 ppm, but with half the intensity found for fully protonated 13. [In principle this species could also be a 1/1 molar mixture of the H$_2$ (13-d_1) and D$_2$ (13-d_3) complexes. However a dihydride complex (13-d_1) cannot be formed because 4, which is the only possible H source for H$_2$ in this rearrangement, has already been consumed (see the derived mechanism shown in Scheme III).] Presumably, this is a result of a random cis addition of the generated HD molecules to 7-d_1.

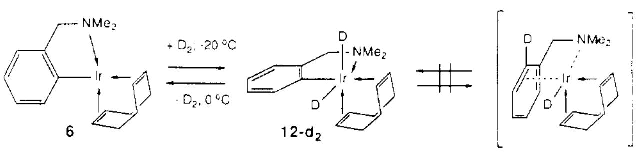

Figure 5. Reaction of Ir^{I}[C$_6$H$_4$(CH$_2$NMe$_2$)-2](COD) (6) with D$_2$.

The reaction of Ir^{I}[C$_6$H$_4$(CH$_2$NMe$_2$)-2](COD) (6) with D$_2$ at −20 °C in CD$_2$Cl$_2$ affords Ir^{III}D$_2$[C$_6$H$_4$(CH$_2$NMe$_2$)-2](COD) (12-d_2) (see Figure 5). When this solution is warmed, the starting complex 6 is recovered with no deuterium incorporated into the 3-position of the aryl ring. This rules out the occurrence of reversible C(aryl)–H elimination/addition reactions in the iridium(III) dihydride complex 12, and therefore probably in 13 and 14 as well.

The mechanisms of the thermally induced and dihydrogen-catalyzed 4/7 and 5/8 isomerizations (shown in Schemes I and III, respectively) are very similar. They include the involvement of some well-defined intermediates, whose nature can be used to explain why the thermally induced isomerization is more effective than the dihydrogen-catalyzed one (which is accompanied by 30% decomposition). For the two processes, the initial activation of 4 and 5 involves oxidative addition of a H–H and a C(alkyl)–H bond, respectively. Subsequent C(aryl)–H reductive elimination takes place affording two completely different intermediates, 16a and 17a. In intermediate 16a (Scheme I), the aryl ligand is bonded to the iridium(I) center by means of a Ir–C(alkyl) σ-bond, probably in combination with an arene π-bond. The presence of the σ-bond probably explains why the aryl ligand at this stadium does not dissociate from intermediate 16a but instead exclusively adds intramolecularly another C(aryl)–H bond via 16b. However, in the other intermediate 17a (Scheme III) the aryl ligand, now present as neutral 1-(Me$_2$NCH$_2$)-3-R-C$_6$H$_4$, is bonded to the iridium center only by weak Ir–N and/or π-arene interactions. It is likely that at this point the observed 30% decomposition to the free arene 1-(Me$_2$NCH$_2$)-3-R-C$_6$H$_4$ and "IrH(COD)" occurs.[14] The weak linkage of the arene ligand in intermediate 17a is demonstrated when PPh$_3$ is present in solution during warmup. This increases the decomposition pathway from 30 to 100%, as PPh$_3$ fully substitutes the arene ligand from intermediate 17a, thereby forming IrH(COD)(PPh$_3$)$_2$. Normally however, in the dominant process (70%) intermediate 17a rearranges to its conformational isomer 17b, whereupon the arene ligand "re-metalates" at the, less sterically hindered, former 3-position of the aryl ligand. This affords the rearranged iridium(III) dihydrides 13 and 14 (which were not actually observed by ^{1}H NMR during

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[14] Although hydride clusters such as Rh$_4$H$_4$(COD)$_4$[15] and Ir$_4$H$_4$(COD)$_4$(C$_3$H$_4$)[16] are known, no such species were observed by ^{1}H NMR during the present experiments.

[15] (a) Schmidt, G. F.; Muetterties, E. L.; Beno, M. A.; Williams, J. M. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1318. (b) Kulzick, M.; Price, R. T.; Muetterties, E. L. *Organometallics* **1982**, *1*, 1256.

[16] Mueller, J.; Menig, H.; Pickardt, J. *Angew. Chem.* **1981**, *93*, 407.

[17] Shapley, J. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 6976.

this conversion), from which subsequent H_2 elimination affords the more stable iridium(I) complexes 7 and 8 (Scheme III).

The thermal reaction of $Ir^{III}H_2[C_6H_2(CH_2NMe_2)_3$-2,4,6](COD) (**15**), which also proceeds via C(aryl)–H reductive elimination, affords the intermediate IrH(COD)[1,3,5-$(Me_2NCH_2)_3C_6H_3$] (cf. **17a**/**b**). All three aryl C–H bonds are now equivalent and equally unfavorable for "re-metalation" due to the steric hindrance of the three bulky CH_2NMe_2 groups. Since "re-metalation" would only result in re-formation of the iridium(III) dihydride complex **15** (a reaction that is obviously thermodynamically unfavorable), the alternative pathway followed is dissociation of the neutral arene ligand 1,3,5-$(Me_2NCH_2)_3C_6H_3$ from the metal center.

Conclusions

Iridium(I) complexes of type $Ir^I[C_6H_2(CH_2NMe_2)$-2-R^1-4-R^2-6](COD) react with H_2 to form the unique octahedral iridium(III) dihydrides $Ir^{III}H_2[C_6H_2(CH_2NMe_2)$-2-$R^1$-4-$R^2$-6](COD), which display interesting reactivity patterns. From these reactions it can be concluded that, without altering the innermost ligand sphere of the metal center, intramolecular steric effects can drastically change the direction of H–H and C–H bond elimination/addition reactions in iridium(III) compounds. Whereas $Ir^{III}H_2$-$[C_6H_2(CH_2NMe_2)$-2-R^1-4-R^2-6](COD) complexes that have a proton as the R^2 group react further by simple H–H elimination, those where R^2 is a bulkier alkyl group react further by an exclusive C(aryl)–H reductive elimination process. Therefore, when discussing the electronic and thermodynamic factors of H–H and C–H bond activation, it is also important to take possible interligand repulsions into account.

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Electronic Structure of Triple-Decker Sandwich Compounds with P_5, P_6, As_5, and C_nH_n as Middle Rings[†]

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Extended Hückel calculations on $CpNiCpNiCp^+$, $CpCoC_6H_6CoCp$, $CpCoC_7H_7CoCp$, $CpVC_6H_6VCp$, $C_6H_6CrC_6H_6CrC_6H_6$, $CpMoP_6MoCp$, $CpCrP_5CrCp$, and $CpMoAs_5MoCp$ (Cp = η^5-C_5H_5) have been carried out to find the relationship of the stability of the metal–ring combination with the number of valene electrons. The electron count varies from 34 electrons to 26 electrons depending on the magnitude of the interactions 4a–e. With the vanadium complex the e_2'' interaction, 4b, is substantial. With P_6, P_5 and As_5 ligands, the a_2'' interaction, 4e, also becomes very strong. $CpMoAs_5MoCp$ leads to a degenerate HOMO with three electrons leading to a distortion of the As_5 ring, with two long and three short As–As bonds. The isoelectronic P_5 compound does not have such a distortion as the HOMO is a nondegenerate MO with only one electron.

Triple-decker sandwiches, **1**, are formally obtained from metallocenes, **2**, by the additional sandwiching with a metal and a ring. The following metal and ring combinations are known among them: metal = V, Cr, Fe, Co, Ni, Mo, Pt; terminal ring = C_5H_5, C_6H_6, $C_2B_2SH_4$, $C_3B_2H_5$; middle ring = C_5H_5, C_6H_6, P_5, As_5, P_6, $C_2B_2SH_4$, $C_4B_2H_5$, $C_3B_2H_5$.[1-16] Table I lists these complexes with the number of valence electrons and the M–M distances wherever known. There are many interesting structural variations in these compounds. The M–M distance falls within the bonding range only with phosphorus and arsenic rings in the middle.[14-16] While most of the triple-decker sandwich compounds with C_nH_n, P_5, and P_6 as middle rings retain local C_n axis, the As_5 ring in $CpMoAs_5MoCp$ has a distorted geometry with two As–As bonds longer than the other three.[16] The structure appears as a combination of As_3 and As_2 as in **3**. The middle As in the As_3 group is farthest from the metals so that an η^4-description is often used for the As_5 ligand.

The number of electrons around the metals also varies considerably. If only the π-electrons of the ligands are included in the electron count, there are 26 electrons in the vanadium complex $C_5H_5VC_6H_6VC_5H_5$ and 34 electrons in the nickel complex $C_5H_5NiC_5H_5NiC_5H_5^+$. There are any number of complexes with intermediate electron counts of 28 and 30 (Table I). Several theoretical studies have

Table I. Currently Known Triple-Decker Sandwich Compounds with Metal-Metal Distances, Number of Valence Electrons, and References

compound	M–M dist[a]	no. of valence electrons	ref
(1) $CpNiCpNiCp^+$	3.580	34	1
(2) $CpCoC_6R_6CoCp$		34	3
(3) $CpVC_6R_6VCp$	3.400	26	2
(4) $C_6H_6CrC_6H_6CrC_6H_6$	3.338	30	4
(5) $CpFe(C_2B_2SR_4)FeCp$	3.236	30	6
(6) $(C_2B_2SR_4)Co(C_2B_2SR_4)Co(C_2B_2SR_4)$		30	7
(7) $CpM(C_3B_2R_5)M'Cp$			
(a) M = Ni, M′ = Ni	3.416	33	8
(b) M = Fe, M′ = Co	3.337	32	8
(c) M = Fe, M′ = Co	3.204	30	8
(d) M = Co, M′ = Co		31	8
(8) $CpCo(C_3B_2R_5)CoCp$	3.140	30	9
(9) $CpRh(C_4B_2R_6)RhCp^{2+}$	3.440	30	10
(10) $CpM(C_3B_2R_5)M'(C_3B_2R_5)$			
(a) M = Co, M′ = Pt		30	11
(b) M = Ni, M′ = Pt		31	11
(c) M = Co, M′ = Ni		30	11
(11) $(C_6H_5R)Fe(C_3B_2H_5)Ni(C_3B_2H_5)$		30	12, 13
(12) $CpMoP_6MoCp$	2.648	28	14
(13) $CpMoAs_5MoCp$	2.762	27	16
(14) $CpCrP_5CrCp$	2.728	27	15

[a] Distances in Å.

[†] Dedicated to Professors P. T. Narasimhan and M. V. George, I. I. T. Kanpur, on their sixtieth birthdays.

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