bears a striking resemblance to coupling reactions reported for the homobinuclear acetylide compound $Fe_2(CO)_6(\mu$-η^2-C≡CPh)(PPh_2).[4] These observations suggest that for certain substrates, in particular acetylenes, attack at a μ-PPh_2 bridge may be a preferred reaction mode. Whether such reactivity precludes the use of phosphido-bridged clusters in the catalytic hydrogenation of substrates remains to be demonstrated.

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Registry No. 1, 82544-75-0; 2, 89486-23-7; 3, 89462-28-2; Co, 7440-48-4; Ru, 7440-18-8; PhC≡CPh, 501-65-5.

Supplementary Material Available: Table of atomic positions, anisotropic thermal parameters, bond lengths and angles, and structure factors (28 pages). Ordering information is given on any current masthead page.

Selective Stoichiometric and Catalytic C–H Bond Cleavage Reactions in Hydrocarbons by Iridium Complexes

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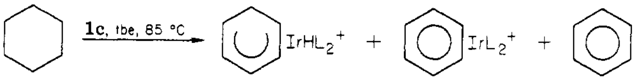
Summary: Complexes of the type $[IrH_2S_2L_2]A$ (S = Me_2CO; L = PPh_3 or $(p\text{-}FC_6H_4)_3P$; A = SbF_6), in the presence of t-BuCH=CH_2 (tbe) at 85–150 °C, can aromatize cyclohexanes to arenes and dehydrogenate cyclopentanes to cyclopentadienyl complexes of the type $[IrCpHL_2]A$ in good to excellent yields. The intermediates $[IrH(\eta^5\text{-}C_6H_7)L_2]A$ and $[Ir(\eta^6\text{-}C_6H_6)L_2]A$ are observed in the cyclohexane case. Cyclooctane is dehydrogenated to $[Ir(cod)L_2]A$, but the addition of base leads to the catalytic formation of free cyclooctene instead. Cyclohexenes can be catalytically aromatized. In some cases, benzene (L = PPh_3) or fluorobenzene (L = $(FC_6H_5)_3P$) is formed in a side reaction involving P–C hydrogenolysis.

The way in which metals break C–H and C–C bonds in hydrocarbons is a topic of current interest.[2-4] In 1979, we described the homogeneous dehydrogenation of various alkanes to give unsaturated metal-bound organic ligands. We proposed that oxidative addition of an alkane C–H bond to the metal was involved.[2d] Several systems have now been developed[3,4] including some in which such an oxidative addition has been directly observed.[4] We now describe a system that allows the stoichiometric aromatization of cyclohexane and the catalytic aromatization of cyclohexene via C–H cleavage reactions.

In our original system,[2d] $[IrH_2S_2L_2]A$ (**1a**, S = Me_2CO, L = PPh_3, A = BF_4) at 80 °C in $C_2H_4Cl_2$ containing t-BuCH=CH_2 (tbe), cyclopentane, cyclooctane, and cycloheptane was converted into $[IrCpHL_2]A$, $[Ir(cod)L_2]A$, and $[Ir(\eta^5\text{-}C_7H_9)HL_2]A$, respectively, but only in moderate yields (12–70%). Other alkanes did not react.

Alkane activation is rare probably because side reactions usually intercept reactive metal fragments. In our own system we now find that reaction with the halocarbon solvent gives ca. 40% of the two binuclear complexes $[HL_2Ir(\mu\text{-}Cl)_2(\mu\text{-}X)IrL_2H]BF_4$[5] (X = H or Cl) among the products; these are inactive for alkane reactions. This prompted us to omit the halogenated solvent and carry out the reactions in neat alkane, containing tbe (tbe:M, 4:1 mole ratio), in a resealable 100-mL glass vessel[6] at 85–150 °C. Rather than **1a** itself, we generally used the related complexes $[IrH_2S_2L_2]A$ (S = Me_2CO, L = PPh_3, A = SbF_6, **1b**; L = $P(p\text{-}FC_6H_4)_3$, A = SbF_6, **1c**). Although the salts **1a–c** *appear* to be entirely insoluble in the alkane, not only are yields greatly improved but also a variety of previously unreactive alkanes now react.

For example, cyclopentane reacts with **1c** at 90 °C for 24 h to give $[IrCpHL_2]A$ (82%). Methyl- and ethylcyclopentane, previously unreactive, now give $[Ir(RC_5H_4)HL_2]A$ (**2**) after 14 h at 120 °C (R = Me, 78%; R = Et, 36%).[7] Cyclohexane, inert under the old conditions, now reacts at 85 °C for 20 h according to eq 1. This is a particularly interesting case in view of the importance of aromatization reactions in reforming. We see an η^5-cyclohexadienyl complex,[8] **3**, probably isolable because it has an 18-electron configuration, as well as the benzene complex **4**[8] and free benzene.[2b] Pure **3** and **4** both pyrolyze (150 °C) to give benzene. At 150 °C reaction 1 gives free benzene (60%), a trace of **4** (5%), and fluorobenzene (0.8 mol/Ir, which must arise from P–C cleavage) after 18 h. We were able to verify that essentially only C_6D_6 (~98% d^6) was formed from C_6D_{12} at 150 °C (GC–MS).



3 (5%) **4** (45%) 32%

(1)

Methylcyclohexane also reacts, but at a higher temperature. At 130 °C, only the cyclohexadienyl complex of type **2** (25%) is formed after 15 h, and at 150 °C for 36 h free toluene (28%) and fluorobenzene (0.8 mol/Ir) are obtained.

It is the decomposition[9] of the complex that probably prevents the systems from being catalytic. Cyclohexene is a sufficiently good ligand to protect the catalyst from

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[6] This consisted of a triple-thickness vessel with a Teflon vacuum stopcock. Our experimental methods were similar to those reported,[2] and organic products were detected by FID–GC (squalane or $AgNO_3$) and identified by GC–MS.

[7] The identity of all products was verified by independent synthesis from the corresponding olefin, and the complexes were fully characterized. **2** (R = Me): ^{1}H NMR $(CD_3)_2CO$ δ −14.6 (t (28), IrH), 1.9 (br s, Me), 5.25 and 5.5 (c, Cp), 7.05, −7.65 (c, Ar). **2** (R = Et): ^{1}H NMR δ 14.3 (t (28), IrH), 1.2 (t (7), Me), 2.4 (c, CH_2), 4.9 and 5.7 (c, Cp), 7.1–7.9 (Ar).

[8] **3**: ^{1}H NMR δ −17.8 (t (22), IrH), 1.4, 2.2, 3.6, 4.0, 5.2 (c, C_6H_7), 7.2 (c, Ar). **4**: ^{1}H NMR δ 6.1 (s, C_6H_6), 7.3 (c, Ar).

[9] Perhaps via the P–C cleavage reaction mentioned above, which may be a general catalyst deactivation pathway in homogeneous catalysis.

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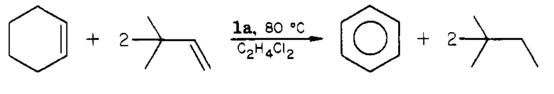
side reactions; **1a** catalyzes the disproportionation of cyclohexene to benzene and cyclohexane at 80 °C. In this reaction the desired arene is accompanied by 2 mol equiv of alkane. The addition of tbe, however, leads to the selective formation of benzene (eq 2). At a substrate:catalyst



(2)

ratio of 100:1, the initial rate is 3 turnovers/h and the conversion is complete in 48 h at 80 °C. Essentially no cyclohexane is formed, showing how selective[5] is **1a** in hydrogenating tbe in preference to cyclohexene. Methylcyclohexene is also catalytically dehydrogenated at 130 °C in $C_2H_4Cl_2$ (sealed tube).

Initial experiments on the effect of base show that catalytic alkane dehydrogenation can occur. For example, cyclooctane gives $[Ir(cod)L_2]A$ (75%, cod = 1,5-cyclooctadiene) with **1c** at 125 °C for 18 h but gives 8 turnovers of free cyclooctene and a trace of cyclooctadienes after 24 h at 140 °C (tbe:Ir = 100:1) with 1.1 mol equiv of 1,8-bis(dimethylamino)naphthalene. The base deprotonates the metal (the protonated amine can be isolated at the end of the reaction), and olefin binding may be weaker to the resulting neutral species and therefore may be released.[10] Cyclohexane gives cyclohexene and benzene (0.4 turnovers each). The deprotonated system is alkane soluble.

While some of the reactions reported above are heterogeneous in the sense that two phases are present, the similarity between this chemistry and that previously reported by us[2d] makes it probable that all these systems are mechanistically alike and in particular do not involve metallic iridium.[12] The salts may well be slightly soluble in the reaction mixture under the reaction conditions.

The degree of dehydrogenation achieved in alkane activation appears to depend on the electron count of the metal species and the binding strength for olefins. The 12-electron strongly binding fragment "IrL_2^+" gives benzene, neutral 12–14-electron fragments tend to give olefins,[10] and 16-electron fragments[4] give the alkyl hydride.

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Registry No. **1a**, 72414-17-6; **1b**, 89509-77-3; **1c**, 89529-62-4; **2** (R = Me), 89509-81-9; **2** (R = Et), 89509-83-1; **3**, 89509-84-2; **4**, 89509-85-3; $[IrCp[P(p\text{-}FC_6H_4)_3]_2]SbF_6$, 89509-79-5; $[Ir(MeC_6H_6)H[P(p\text{-}FC_6H_4)_3]_2]^+$, 89509-86-4; $[Ir(cod)[P(p\text{-}FC_6H_4)_3]_2]SbF_6$, 89509-87-5; ±-BuCH=CH$_2$, 558-37-2; ethylcyclopentane, 1640-89-7; cyclohexane, 110-82-7; methylcyclohexane, 108-87-2; cyclopentane, 287-92-3; methylcyclopentane, 96-37-7; cyclohexene, 110-83-8; methylcyclohexene, 1335-86-0; cyclooctane, 292-64-8; 1,8-bis(dimethylamino)naphthalene, 20734-58-1; benzene, 71-43-2; chlorobenzene, 108-90-7; toluene, 108-88-3; cyclooctene, 931-88-4.

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(10) One equivalent of base is required for full activity, but up to 10 equiv did not inhibit the dehydrogenation reaction. These simple dehydrogenations of alkanes to olefins by neutral highly coordinatively unsaturated species and tbe seem to be quite general.[3] Hugh Felkin informs us (personal communication, 1983) that $RuH_4(PPh_3)_3$ and $IrH_5(PPh_3)_2$ are active, and we have more recently found $OsH_4(p\text{-}FC_6H_4)_3P)_3$ is also effective.[11]

(11) Crabtree, R. H.; Davis, M. W., unpublished observations, 1983.

(12) The reactions described proceed even in the presence of metallic mercury, a poison for heterogeneous catalysts,[13] suggesting that metallic iridium is not involved in these dehydrogenations.

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Electron Transfer vs. Hydride Transfer in the Reduction of $[C_5R_5Fe(dppe)(CO)]^+PF_6^-$ (R = H or CH_3) by $LiAlH_4$[1]

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Summary: $LiAlH_4$ reacts with $[C_5Me_5Fe^{II}(dppe)(CO)]^+PF_6^-$, **4**, at −80 °C to give $C_5Me_5Fe^{II}(dppe)(CO)(H)$, **5**, via an electron-transfer mechanism and subsequent H atom abstraction by the 17-electron intermediate $[C_5Me_5Fe^{I}(dppe)(CO)]$; this highly unstable and reactive species can also be generated by one-electron reduction of **4** (K mirror or Na/Hg) and gives **5** on Na/Hg/OH$^-$.

Intermolecular reduction by main-group hydrides of CO activated in transition-metal complexes is a widely recognized model for the important Fischer–Tropsch process.[2-6] Yet the site of hydride transfer to the transition-metal carbonyl complex is not always the carbonyl carbon; it may in some instances be an ancillary organic ligand or the metal itself. The rules of Green et al. have proposed priorities in this respect, based on the principle that nucleophilic attack on organotransition-metal cations is charge controlled.[7] A possible alternative that we wish to illustrate here is the electron-transfer (ET) pathway, followed by H atom abstraction from the hydride or the medium (Scheme I). Recently, we showed that the ET mechanism may occur in the reduction of d^6 and d^7 organoiron complexes by $NaBH_4$ and $LiAlH_4$,[8] but this study was limited to sandwich complexes.

It is already known from the recent work by Davies et al. that $LiAlH_4$ reduction of $[C_5H_5Fe^{II}(dppe)(CO)]^+PF_6^-$, **1**, in THF yields the formyl complex $C_5H_5Fe^{II}(dppe)(CHO)$, **2**, at −80 °C. We have verified this finding and noticed that **2** is stable up to 0 °C (by ^1H and ^{31}P NMR), giving then *inter alia* $C_5H_5Fe^{II}(dppe)(CO)(H)$,[9] **3**. Reduction of $[C_5Me_5Fe^{II}(dppe)(CO)]^+PF_6^-$, **4**,[10] under identical conditions at −80 °C immediately gives the new, pale yellow hydride complex $C_5Me_5Fe^{II}(dppe)(CO)(H)$, **5**.[11] No

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