Mechanism of Cyclometalation of Tris(trimethylphosphine)neopentyliridium(I)

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The mechanism of the known cyclometalation of the R group of L_3IrR (L = PMe_3; R = CH_2CMe_3 (1), CH_2SiMe_3 (2)) to form fac-$L_3Ir(H)(\eta^2\text{-}CH_2EMe_2CH_2)$ (E = C (3), Si (4)) has been investigated. The reactions of both 1 and 2 are first order and show no inhibition by high concentrations of added L. Activation parameters are found to be as follows: formation of 3 at 0 °C $\Delta H^* = 17.8$ (0.8) kcal/mol and $\Delta S^* = -10.0$ (2.9) eu; formation of 4 at 45 °C, $\Delta H^* = 21.8$ (0.2) kcal/mol and $\Delta S^* = -9.8$ (0.6) eu. Reaction of $L_3Ir[CH_2Si(CD_3)_3]$ (2-d_9) reveals an isotope effect of 3.2 on the observed rate. Reactions of $L_3Ir[CH_2E\text{-}(CH_3)(CD_3)_2]$ (1-d_6, 2-d_6) give nonrandom distributions of deuterium in cyclometalated products 3-d_9 and 4-d_9 that do not change with time at temperatures of up to 80 °C. At 95 °C the deuterium becomes randomly distributed between the CH_2 and CH_3 groups of the ligand. When heated at 95 °C with a large excess of $P(CD_3)_3$ (L'), 3 and 4 incorporate L' without any scrambling of deuterium to or from the solvent or into the alkyl or hydride ligands. L' is incorporated three at a time to go directly to $(L')_3Ir(H)(\eta^2\text{-}CH_2EMe_2CH_2)$ (3-d_{27}, 4-d_{27}) only; no d_9 or d_{18} species are detected by ^{31}P NMR spectroscopy. From the rates of 95 °C and from the activation parameters given above, values of ΔG_{reacn} for the cyclometalations of 1 and 2 are calculated to be -7.7 (2.0) and -4.6 (0.3) kcal/mol, respectively, at 95 °C. These data are most consistent with a mechanism for the reversible cyclometalation that involves direct, concerted oxidative addition and reductive elimination of the C–H bond interconverting square-planar Ir^I and octahedral Ir^{III} centers without any L dissociation.

Introduction

A number of examples of intermolecular C–H "activation" (oxidative addition) that give characterizable hydrido(hydrocarbyl)metal (MHR) products from hydrocarbons and soluble metal complexes have arisen in recent years,[1,2] and it has become clear that the thermodynamic stability of such products can be substantial.[1] Of particular potential interest are the oxidative-addition and reductive-elimination reactions of C(sp³)–H bonds interconverting square-planar d⁸ and octahedral d⁶ complexes (eq 1), but there are still very few well-defined examples of this

(1)

L = a variety of neutral and / or anionic ligands
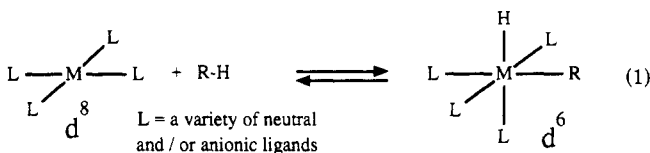
reaction in either direction.[3] However, there is mounting

evidence that such interconversions should have a significant kinetic barrier when they occur in a single step.[3c,f,4] Cyclometalation (oxidative addition of a C–H bond of a ligand to form a chelate complex) is much more common than intermolecular C–H oxidative addition,[5] and yet with few exceptions[3c,d] mechanisms of this reaction have not been extensively studied either. There may be substantial similarities between the intramolecular and intermolecular reactions, so the study of mechanisms of cyclometalation may give valuable insight into intermolecular C–H activations.

In 1981, Tulip and Thorn reported[6] the cyclometalation reaction of eq 2. The neopentyl intermediate was detected

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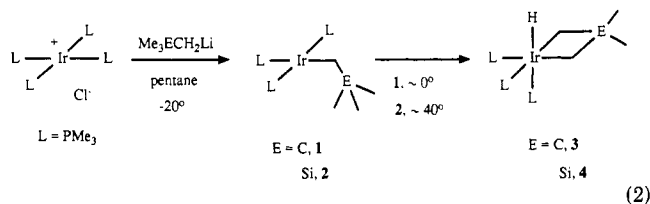
as a transient orange solution, and the (trimethylsilyl)-methyl species was characterized by ¹H and ³¹P NMR spectroscopy but not isolated. No mechanistic investigations were undertaken.

Molecules such as 1 and 2 may offer the possibility of carrying out systematic studies of cyclometalations, particularly since this system should be amenable to variation of both L and the alkyl ligands, and the reaction is reported to be well-behaved.[6] As a first step in such an investigation, we have carried out a careful examination of the

(1) (a) Crabtree, R. H. *Chem. Rev.* 1985, *85*, 245–269. (b) Green, M. L. H. *Pure Appl. Chem.* 1978, *50*, 27–35. (c) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* 1978, *100*, 4080–4089. (d) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* 1983, *105*, 3929–3939. (e) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* 1983, *105*, 7190–7191. (f) Wenzel, T. T.; Bergman, R. G. *J. Am. Chem. Soc.* 1986, *108*, 4856–4867. (g) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* 1988, *110*, 1449–1462. (h) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* 1986, *108*, 4814–4819. (i) Harper, T. G. P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *J. Am. Chem. Soc.* 1988, *110*, 7915–7916.

(2) There is also a class of C–H "activations" that involve metathetical exchange between M–C and C–H bonds: (a) Watson, P. L. *J. Am. Chem. Soc.* 1983, *105*, 6491–6493. (b) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* 1984, *106*, 2214–2216. (c) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* 1987, *109*, 203–219.

(3) (a) Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* 1982, *104*, 6994–7001. (b) Cameron, C. J.; Felkin, H.; Fillebeen-Khan, T.; Forrow, N. J.; Guittet, E. *J. Chem. Soc., Chem. Commun.* 1986, 801–802. (c) Foley, P.; DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* 1980, *102*, 6713–6725. (d) DiCosimo, R.; Moore, S. S.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* 1982, *104*, 124–133. (e) Werner, H.; Gotzig, J. *J. Organomet. Chem.* 1985, *284*, 73–93. (f) Shinomoto, R. S.; Desrosiers, P. J.; Harper, T. G. P.; Flood, T. C. *J. Am. Chem. Soc.* 1990, *112*, 704–713. (g) The complex Pt(PPhMe₂)₂(CH₂SiMe₃)₂ undergoes an unusual intramolecular rearrangement that may involve a cyclometalation analogous to that of the Whitesides complex 7 (eq 4³ᶜ), but in any event, prior dissociation of phosphine is also required: Thomson, S. K.; Young, G. B. *Organometallics* 1980, *8*, 2068–2070.

(4) Much information regarding the degree of coordination of metals in reactions with saturated hydrocarbons has come from investigations of reductive eliminations forming C–H and C–C bonds rather than oxidative additions: (a) Milstein, D. *J. Am. Chem. Soc.* 1982, *104*, 5227–5228. (b) Basato, M.; Longato, B.; Morandini, F.; Bresadola, S. *Inorg. Chem.* 1984, *23*, 3972–3976. (c) Basato, M.; Morandini, F.; Longato, B.; Bresadola, S. *Inorg. Chem.* 1984, *23*, 649–653. (d) Clark, H. C.; Manzer, L. E. *Inorg. Chem.* 1973, *12*, 362–368. (e) Brown, M. P.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* 1974, 2457–2465. (f) Roy, S.; Puddephatt, R. J.; Scott, J. D. *J. Chem. Soc., Dalton Trans.* 1989, 2121–2125.

(5) Webster, D. E. *Adv. Organomet. Chem.* 1977, *15*, 147–188.

(6) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* 1981, *103*, 2448–2450.

Table I. Rates of Cyclometalation of L$_3$IrCH$_2$CMe$_3$ (1) and L$_3$IrCH$_2$SiMe$_3$ (2) under Various Conditions

starting material	temp, °C	k_{obsd}, s^{-1} (sd^a)
1	-18	2.42 × 10^{-5} (0.15)
1	0	2.04 × 10^{-4} (0.07)
1	12	1.09 × 10^{-3} (0.05)
1	18	1.98 × 10^{-3} (0.24)
2	25	1.40 × 10^{-5} (0.02)
2	35	4.63 × 10^{-5} (0.07)
2	45	1.48 × 10^{-4} (0.03)
2	65	1.08 × 10^{-3} (0.03)
2-d_9	50	7.57 × 10^{-5} (0.15)
1 + PMe$_3^b$	0	2.16 × 10^{-4} (0.42)
2 + PMe$_3^c$	45	1.08 × 10^{-4} (0.15)

^{a} Standard deviation. ^{b} [L] = 2.4 M. ^{c} [L] = 0.13 M.

mechanism of the reaction of the parent system where L = PMe$_3$. We report out initial results here.

Results and Interpretations

Parent complexes 1 and 2 were prepared as shown in eq 2 from the corresponding lithium reagent and a suspension of [L$_4$Ir$^+$]Cl$^-$ (L = PMe$_3$) in pentane solvent at -20 °C as reported by Tulip and Thorn.[6] Both are formed over a period of 1 h at that temperature. The carbon analogue 1 undergoes cyclometalation slowly at -20 °C and rapidly at 0 °C to form 3. Compound 2 is stable indefinitely at -20 °C either as a solid or in solution. It cyclizes slowly at 25 °C and cyclizes at a conveniently measurable rate at 45 °C to form 4. It was possible to isolate crystals of 2 from its pentane solutions at -20 °C. Use of either 2 as the crystalline form or 2 in solutions in which it was prepared made no difference in the outcome of any experiments. Deuterated materials 1-d_6, 2-d_6, and 2-d_9 were prepared in the same fashion as for 1 and 2 from the corresponding lithium reagents prepared by standard techniques (see Experimental Section).

	R
1-d_6	-CH$_2$C(CH$_3$)(CD$_3$)$_2$
2-d_6	-CH$_2$Si(CH$_3$)(CD$_3$)$_2$
2-d_9	-CH$_2$Si(CD$_3$)$_3$
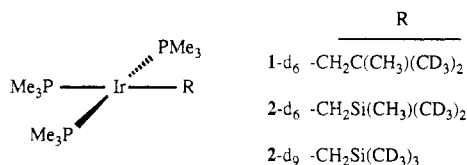
It is important for the discussion below to note that the rate of exchange between 1 or 2 and free L is much faster than cyclization. For example, the ^{31}P NMR spectrum of a solution of 1 with excess L at 0 °C showed only a broadened peak for free L with its chemical shift moved downfield toward the position of the ligand resonances of 1, and the resonances of 1 were absent. However, as 1 was converted to 3 in this sample, the ligands of 3, not exchanging with free L at this temperature (see below), exhibited resonances that were intense and sharp. At 40 °C the ^{31}P spectrum of 2 and free L showed total coalescence, while the resonances of newly formed 4 in the sample were sharp.

Kinetics of the cyclometalation of 1 and 2 were followed by ^{31}P NMR spectroscopy. For example, for 2, the doublet at δ -24.3 and the triplet at δ -31.2 were cleanly converted to a doublet at δ -57.4 and a triplet at δ -59.8 characteristic of 4. The rates of cyclometalation of 1 and 2 were measured at four temperatures each (Table I). These data yield the activation parameters shown in Table II.

Two particularly noteworthy points are to be made about the data in these tables. First, with use of the activation parameters in Table II, the rate constant for cyclometalation of 2 at 50 °C can be calculated to be 2.44 × 10^{-4} s^{-1}. This compared to the rate constant for reaction

**Table II. Activation Parameters for the Cyclometalation of L$_3$IrCH$_2$CMe$_3$ (1) and L$_3$IrCH$_2$SiMe$_3$ (2)^a**

starting material	E_a, kcal/mol	ln A	$\Delta H^\ddagger$, kcal/mol [T, °C]	$\Delta S^\ddagger$, eu [T, °C]
1	18.3 (0.8)	25.4 (1.5)	17.8 (0.8) [0]	-10.0 (2.9) [0]
2	21.8 (0.2)	25.6 (0.3)	21.1 (0.2) [45]	-9.8 (0.6) [45]

^{a} Standard deviations in parentheses.

Scheme I
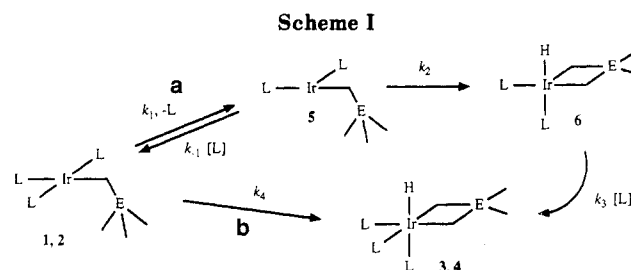
of 2-d_9 at 50 °C yields a kinetic isotope effect, KIE, of k_H/k_D = 3.2 on k_{obsd}. Second, reactions of 1 at 0 °C without added L and in the presence of 2.4 M added L show no significant difference in rates. Similarly, cyclizations of 2 at 45 °C with and without added L show essentially the same rate. Clearly, there is no inhibition of unsaturated intermediates upon addition of L.
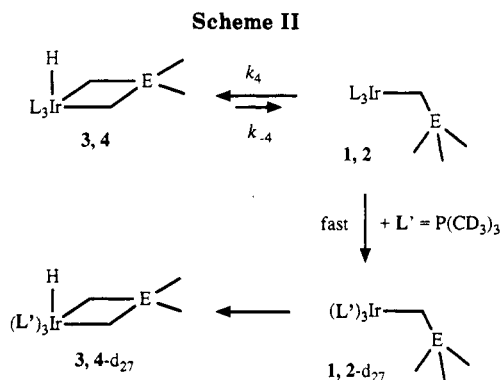
The reaction was tested for reversibility by thermolysis of the hexadeuterated species 1-d_6 and 2-d_6. If the cyclometalation were not reversible, then the mixture of isotopic isomers shown in eq 3 would be formed. Since we

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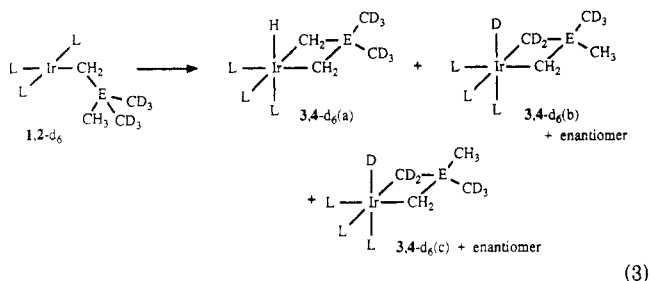
have seen that there is a KIE of 3.2 on this reaction, there should be more 3- or 4-d_6(a) isomer than the d_6(b) or d_6(c) isomers, and the integral ratios for the ^{1}H NMR resonances for the methylene/methyl groups would be 2.8/1. If the reaction were reversible, then the ^{1}H in the ligand would become randomly located and the ratio should be 4/6 or 0.67. The ^{1}H NMR spectrum of 4-d_6 revealed a methylene/methyl ratio of 2.8. Thus, since the H and D were not randomly distributed, these experiments with d_6 substrates offer good evidence that the cycloaddition is irreversible at these temperatures, and the isotope effect measured must be kinetic and not thermodynamic.

Only the kinetic (nonrandom) products of eq 3 were visible by NMR spectroscopy for prolonged times at temperatures of up to 80 °C. However, at 95 °C, randomization of the deuterium label became evident since the methylene/methyl integral ratio diminished smoothly. While the deuterium migrated throughout the hydrocarbon ligand, there was no exchange with deuterated or nondeuterated solvent or into the phosphine ligand.

The two most probable mechanisms for the cyclometalation are shown in Scheme I. Mechanism a, since intermediates 5 and 6 would be present in very low concentration, would be expected to obey the usual, simple rate law of $-d[1]/dt = k_{obsd}[1]$ (or similarly for 2), wherein $k_{obsd} = k_1k_2/(k_{-1}[L] + k_2)$. Thus, if k_2 were much larger than $k_{-1}[L]$, the k_1 step would be rate-determining and there would be no inhibition by added phosphine. As

Scheme II

Figure 1. Possible isomers resulting from random substitution of L (P(CH$_3$)$_3$) and L' (P(CD$_3$)$_3$) in 3 (E = C) and 4 (E = Si).

Scheme III

Scheme IV

mentioned above, no phosphine inhibition is observed. However, if k_1 were rate-limiting, then there should be no primary KIE on k_{obsd}. This last supposition is contrary to fact since, as noted above, k_{obsd} exhibits an isotope effect of 3.2. This contradiction rules out the dissociative path, path a of Scheme I. Thus, path b, direct oxidative addition of the C–H bond to square-planar 1 or 2 without ligand dissociation, is the most probable mechanism for these cyclometalations.

If the rate for the reverse reaction, k_{-4}, could be measured, then ΔG_{reacn} could be calculated from the kinetic data. As mentioned above, the label scrambling of 3-d_6 and 4-d_6 above ca. 95 °C indicates reversal, but calculation of k_{-4} from these data would be tedious. It was found that the rate could be determined by monitoring the exchange of 3 or 4 with free P(CD$_3$)$_3$ (L'). The experiment depends on the ability of ^{31}P NMR spectroscopy to distinguish between L and L'. Fortunately, there is a large isotope effect on the ^{31}P chemical shifts. For example, uncoordinated L appears at δ –62.3 and L' at –65.2. The difference is not quite as large for coordinated L, but it is still pronounced, with $\Delta\delta$ generally close to 2 ppm for Ir–L vs Ir–L', so incorporation of L' into any of the complexes is easily detected. The experiment also relies on an observation made above: when 1 or 2 is treated with a large excess of L', it immediately fully exchanges all three ligands with the labeled material. Thus, complete exchange of 1 or 2 with L' and then recyclization should yield 3-d_{27} or 4-d_{27}. This proposed sequence is outlined in Scheme II.

The procedure involves heating 3 or 4 in the presence of a large excess of L' and determining the rate of incorporation of L' to form 3-d_{27} or 4-d_{27}. It is to be noted that this procedure does not generate any partially exchanged species such as 3-d_9 or 3-d_{18}. More about this is said below. Since k_{-4} is the rate–determining step in the ligand exchange of 3 and 4 and since all three phosphine ligands exchange at one time for each molecule, it is straightforward to measure the rate constant k_{-4}. These are (4.13 (0.52)) × 10^{-5} s^{-1} for 3 and (2.54 (0.14)) × 10^{-5} s^{-1} for 4, or $\Delta G^{\ddagger}$(95 °C) = 29.1 (0.1) kcal/mol for 3 and 29.4 (0.1) kcal/mol for 4. From the activation parameters in Table II, we can calculate the free energy of activation at the same temperature for the cyclometalation, k_4, and $\Delta G^{\ddagger}$(95 °C) = 21.4 (1.9) kcal/mol for 1 and 24.8 (0.2) kcal/mol for 2. It follows that ΔG_{reacn} (95 °C) for the cyclometalation reaction is –7.7 (2.0) kcal/mol for 1 and –4.6 (0.3) kcal/mol for 2.

Incidentally, the above ligand-exchange experiment offers some evidence against a third mechanism for the cyclometalation. Literature precedents[4] (see Discussion) suggest that a C–H oxidative addition or reductive elimination as shown in eq 1 should proceed via prior ligand dissociation, even in the case of intramolecular activa-
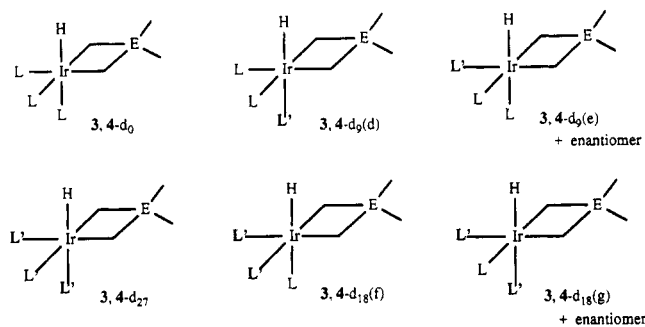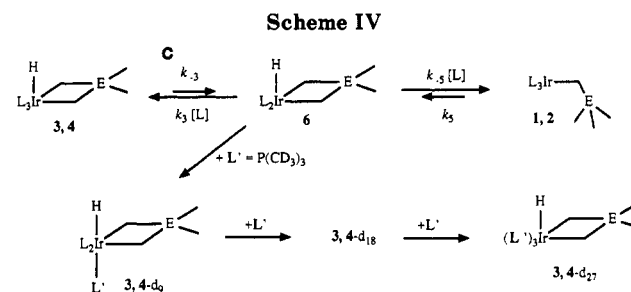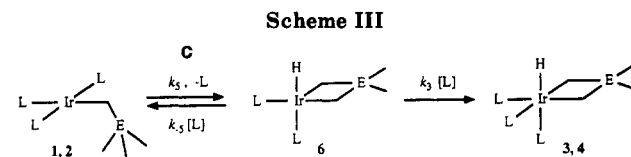
tions.[3c,d] In light of such accumulating precedents, the one-step mechanism (b) is somewhat surprising. Although unconventional, the mechanism of path c in Scheme III is a possibility. Perhaps as the phosphine would dissociate, the interaction of the C–H bond with the metal would already be so intimate that this activation would occur concurrently, and so the initial step would proceed directly to the five-coordinate 6. If k_5 were rate-determining (i.e., if $k_3 \gg k_{-5}$), path c would be expected to show no inhibition by L and to exibit the full isotope effect of C–H activation in k_{obsd}, so path c would be indistinguishable from path b on the basis of these data.

If $k_3 \gg k_{-5}$, then the L' exchange experiment with 3 or 4 described above could distinguish between paths b and c. As shown in Scheme II, exchange by path b should occur only three L' groups at a time. Thus, as the exchange proceeds, only 3 and 3-d_{27} would be present; the ^{31}P NMR doublet at δ –59.1 and the triplet at δ –59.7 would move to δ –61.2 and –61.7, respectively.

As shown in Scheme IV, by path c a single L would be lost from 3 to form 6 and then L' would rapidly be reassociated, generating 3-d_9. Exchange of ligands in 3 would therefore take place one L' group at a time, and 3-d_9 and 3-d_{18} would build up during the experiment. If the exchange were stereospecific, the process would be obvious since either the ^{31}P doublet at δ –59.1 or the triplet at δ –59.7 would move to higher field, but not both at the same rate. If the exchange were stereorandom, then at partial reaction the mixture of d_0-, d_9-, d_{18}-, and d_{27}-containing 3 shown in Figure 1 would be present. Analysis of such a mixture is possible from its ^{31}P NMR spectrum. Isomers 3-d_9(e) and 3-d_{18}(g) contain two normally equivalent ligands trans to the Ir–C bonds that are now inequivalent, and their coupling becomes visible. To determine the coupling constant, standard samples of mixtures of the L/L' isomers of 3 and 4 were prepared by carrying out the
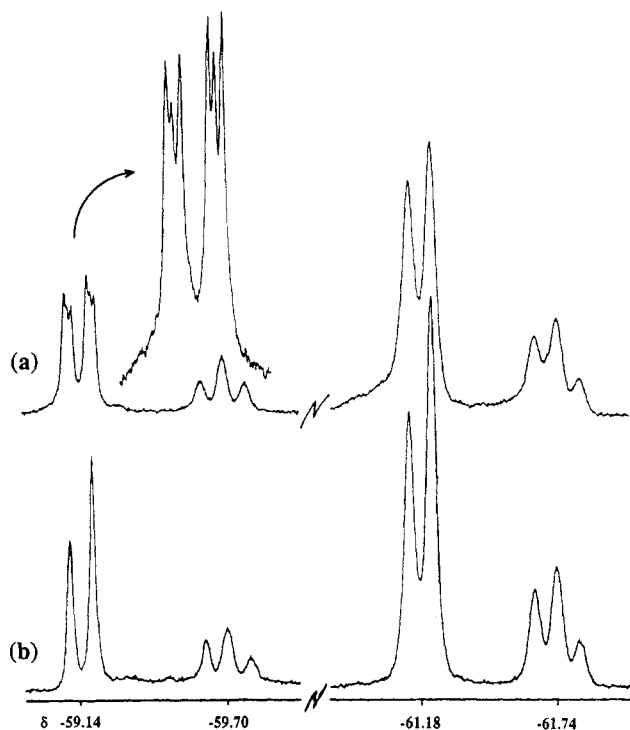
Figure 2. $^{31}P\{^1H\}$ NMR spectra of $(L')_nL_{3-n}Ir(H)(\eta^2\text{-}CH_2CMe_2CH_2)$ (3; L = $P(CH_3)_3$; L' = $P(CD_3)_3$) as (a) a randomly substituted synthetic mixture of d_0, d_9, d_{18}, and d_{27} isotope isomers as shown in Figure 1 and (b) the mixture of isotope isomers resulting from heating 3 at 95 °C in cyclohexane in the presence of excess L', after ca. 70% exchange.

alkylation of $[L_4Ir]Cl$ to form 1 and 2 in the presence of a large excess of a 1/2.5 mixture of L and L'. Complete equilibration of the square-planar molecules with the ligand mixture is much more rapid than cyclometalation, and so the cyclometalated products contain randomly positioned L and L'. A ^{31}P NMR spectrum of the mixture of isomers of 3 is shown in Figure 2a. The cis coupling is clearly visible from the δ -59.1 doublet, since it is now further split into a doublet with $J_{PP(cis)}$ = 4.2 Hz. Figure 2b shows the results of heating $3\text{-}d_0$ with a large excess of L' at 95 °C in cyclohexane at ca. two-thirds reaction. The half-height width of the low-field doublet is 3.3 Hz; any significant quantity of isomers $3\text{-}d_9(e)$ and $3\text{-}d_{18}(g)$ would be clearly visible at this stage of the reaction. The absence of any detectable quantities of mixed isomers of 3 is most consistent with a concerted path, path b, for the 1–3 interconversion. The same experiments with 4 give the same results, although the cis coupling of the random mixture of partially exchanged 4 is not as well-resolved as is that of 3.

The possibility exists that mechanism c could operate but with $k_{-5} \gg k_3$. Such a situation would be consistent with exchange of L' into 4 three at a time. However, we believe that this is less likely than $k_3 \gg k_{-5}$ for two reasons. First, the lack of scrambling of deuterium within the alkyl ligand in the conversion of $1\text{-}d_6$ or $2\text{-}d_6$ to $3\text{-}d_6$ or $4\text{-}d_6$ below 80 °C suggests that k_5 and not k_3 would be rate limiting if mechanism c were operative. Although possible, it seems unlikely that intermediate $6\text{-}d_6$ would form reversibly from $1\text{-}d_6$ or $2\text{-}d_6$ and still not lead to scrambling. Secondly, intuitively it seems unlikely that simple recoordination of L by attack on intermediate 6 to form 1 or 2 would be slower than recoordination of L with concomitant reductive elimination of the C–H bond to give 3 or 4. Additionally, the isotope effect of 3.2, reasonably large for a nonlinear transition state, seems more likely to be associated with the C–H bond-breaking step, k_5, than with the ligand

uptake (with $k_{obsd} = k_5k_3/k_{-5}$), but this is not a convincing point since the equilibrium isotope effect on k_5/k_{-5} could be significant.

Discussion

There are a number of precedents[3c,f,g,4] which suggest that the oxidative addition and reductive elimination of C–H bonds interconverting d^8 square planar and d^6 octahedral species as shown in eq 1 should preferentially proceed via a coordinately unsaturated intermediate; that is, a three-coordinate, 14-electron complex and a five-coordinate, 16-electron species. Indeed, we are unaware of any established example of an intermolecular $C(sp^3)$–H oxidative addition directly to a square-planar complex. The work of Whitesides[3c] (eq 4) clearly establishes in the

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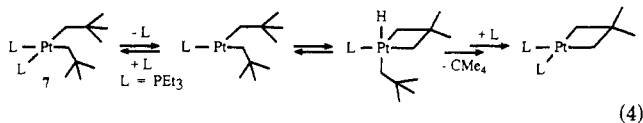
case of 7, even for cyclometalation of a neopentyl group, this unsaturation criterion must be met. This precedent was the motivation for our detailed examination of the Tulip and Thorn reaction. When our initial results pointed to a direct oxidative addition without ligand dissociation, we decided to check even the unconventional mechanism of path c in Scheme IV. Our results clearly establish that in the cases of 1 and 2 no unsaturation is required beyond the usual 16-electron configuration.

It is generally believed that the essential features of the oxidative-addition reaction of a C–H bond to a metal are as follows.[7] The metal is required to possess a vacant, acidic (low–lying) molecular orbital (MO) of σ symmetry and a basic (filled), π-symmetry MO. The initial interaction of the hydrocarbon with the metal center is presumably that of electron density donation from a C–H σ bond to the acidic metal σ MO. As this acid–base coordinate bonding develops and the hydrocarbon comes closer to the metal, the metal π-symmetry basic orbital begins to donate electron density back into the empty C–H antibonding orbital. These two interactions lead to the formation of the two quasi-"symmetric and antisymmetric" σ-bonding combinations of the C–M–H bonds. In a square-planar complex, the two degenerate filled orbitals, essentially d_{xz} and d_{yz}, are the reactive π-symmetry orbitals. The essentially p_z orbital, which is colinear with the filled d_{z^2} orbital, is the reactive acidic σ orbital. In this case, the acid–base interaction of the empty metal p_z orbital with the C–H σ bond is offset by the repulsive interaction of that σ bond with the filled metal d_{z^2} orbital.[7] Thus, the hydrocarbon cannot get close enough to the metal for back-donation from the metal π-donor orbital to the C–H antiboding orbital to become important, and the oxidative addition has a substantial barrier.

Complexes 1 and 2, being very congested, are probably significantly distorted from square planarity. Substantial puckering is evident in the X-ray crystal structure of $[(Me_3P)_4Rh]^+Cl^-$; which is distorted toward tetrahedral geometry (the two *trans*-P-Rh-P angles are 148 and 151°),[8] and $[(MePh_2P)_4Ir]^+BF_4^-$ is similarly distorted (both *trans*-P-Ir-P angles are 151°).[9] A closer analogue of $L_3IrCH_2EMe_3$ is Whitesides' $(Et_3P)_2Pt(neopentyl)_2$ (7),

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wherein the dihedral angle between the P–Pt–P and C–Pt–C planes is 19°.[10] Thus, one may assume that 1 and 2 are significantly distorted, and this deformation may in part account for their facile cyclometalation. Also, the forced propinquity of the C–H bond to the metal would result in the penetration of that bond beyond the zone of net repulsive interaction between the filled metal d_{z^2} orbital and the C–H bonding electrons to the point that π back-bonding to the CH antibonding orbital could become important, and the oxidative addition could proceed.

Since the Si–C bond is ca. 0.3 Å longer than the C–C bond, the neopentyl group of 1 will be held closer to the crowded metal center than will the CH_2SiMe_3 group of 2, and 1 will be more congested and probably more distorted. Thus, the greater reactivity of 1 over that of 2 may be the result of the greater distortion of 1 and/or the greater penetration of the C–H bond into the orbitals of the iridium. Additionally, an electronic effect of Si on the C–H bond being activated or on the activation transition state could be significant. We cannot determine the relative importance of these factors.

The reasons 1 and 2 directly cyclometalate while 7 requires ligand dissociation are not yet clear. One possibility is that the lower electronegativity and lower oxidation state of Ir(I) vs that of Pt(II) may make iridium a significantly better π base, enhancing that critical component of the C–H oxidative-addition transition state for Ir. In this connection, it is noteworthy that our data indicate that L_4Os also very readily cyclometalates to form *fac*-$(Me_3P)_3Os(H)(\eta^2\text{-}CH_2PMe_2)$ without dissociation of L.[3f,11]

Our knowledge of ΔG_{reacn} for these cyclometalations allows a very qualitative calculation of the sum of the bond energies of Ir–H and Ir–C $(D_{Ir-H} + D_{Ir-C})$ for this system. If we assume that $\Delta S^{\ddagger}$ for the 1-2 conversion is essentially ΔS_{reacn}, then ΔH_{reacn} at 95 °C is ca. –11 kcal/mol for 1 and –8 kcal/mol for 2. The ring strain of 3 or 4 is not known, but estimates for $(Et_3P)_2Pt(\eta^2\text{-}CH_2CMe_2CH_2)$[3d] and $(py)_2ClPt_2(\eta^2\text{-}CH_2CH_2CH_2)$[12] are <5 and ca. 12 kcal/mol, respectively. If we arbitrarily assign ring strains of 12 and 5 kcal/mol to 3 and 4, respectively, and use the standard $D_{1°(C-H)}$ of 98 kcal/mol, the sum of $D_{Ir-H} + D_{Ir-C}$ is found in the range of 111–121 kcal/mol for 3 and 4. Bergman et al. have found $D_{Ir-H} + D_{Ir-C}$ to be in the range of 125–130 kcal/mol for $Cp^*Ir(PMe_3)(H)(cyclohexyl)$.[13] It is difficult to compare these numbers because of possible differences in steric effects, imprecise knowledge of ring strains, and differences in $D_{1°(C-H)}$ and $D_{2°(C-H)}$.

In summary, in contrast to the case for $(Et_3P)_2Pt(neopentyl)_2$, the complexes $(Me_3P)_3Ir(CH_2EMe_3)$ (E = C, Si) do not require the initial dissociation of a ligand to undergo cyclometalation. This system should be well suited to the investigation of the rates and equilibria of intramolecular oxidative addition of C–H bonds as a function of the ancillary ligands. Such investigations are underway.

Experimental Section

General Comments. Chemical shifts of NMR spectra, recorded on a 270-MHz or on a 360-MHz FT spectrometer, are reported in ppm (δ) downfield from tetramethylsilane for ${}^1H$ and from internal or external PMe_3 (L), which is assigned a value of δ –62.3 ppm with respect to 85% aqueous H_3PO_4, for ${}^{31}P$ spectra; all coupling constants are apparent with absolute values reported

in Hz. All manipulations and reactions involving organometallic compounds were carried out in evacuated sealed tubes, under an atmosphere of dinitrogen purified over reduced copper catalyst and in flamed-out glassware with use of standard Schlenk techniques, or in a dinitrogen atmosphere box. THF and Et_2O were distilled under a dinitrogen atmosphere from purple solutions of sodium/benzophenone immediately prior to use. Pentane and hexane were washed with portions of concentrated H_2SO_4 until the acid remained colorless, were treated with aqueous $NaHCO_3$, anhydrous $MgSO_4$, and CaH_2, and then were distilled from sodium/benzophenone. Literature preparations were used for $[L_4Ir]Cl$[14] and trimethylphosphine-d_9 (with CD_3MgI).[15]

Preparation of Neopentyltris(trimethylphosphine)iridium(I) (1) and Its Cyclization to (η^2-2,2-Dimethyltrimethylene)hydridotris(trimethylphosphine)iridium(III) (3). Compound 1 reacts at a significant rate upon storage at –20 °C either as a glass or in solution, and so it was stored at –78 °C or used immediately. A centrifuge tube was charged with 404 mg (0.76 mmol) of $[L_4Ir]Cl$ and 81 mg (1.0 mmol) of neopentyllithium and placed in a –78 °C bath, and 35 mL of pentane was added via syringe. The tube was placed in an ice/salt bath, and the contents were stirred at ca. –15 °C for 5 h. The solution was filtered through Celite with use of a jacketed fritted filter at –78 °C. A gauze-wrapped cannula was bathed with –78 °C acetone during all solution transfers. The filtered orange solution was pumped free of solvent while in a –20 °C bath. Pentane was added, and the solution was divided among six 9-mm NMR tubes in a –78 °C bath with use of the cold cannula technique just described. The tubes were individually transferred to the vacuum line, sealed, and then stored at –78 °C until used. With these techniques, it was possible to obtain solutions of 1 that were ca. half-converted to product. ${}^{31}P\{{}^1H\}$ NMR (pentane): δ –24.3 (d, 2 P, J_{pp} = 20 Hz), –31.0 (t, 1 P).

Cyclometalation of 1 was accomplished by leaving an NMR tube containing a pentane solution of 1 as prepared above at a temperature of –20 °C or above. The reaction was essentially quantitative by NMR spectroscopy. The ${}^1H$ and ${}^{31}P\{{}^1H\}$ NMR spectra of product 3 agreed with published[6] spectra. ${}^{31}P\{{}^1H\}$ NMR (pentane): δ –59.1 (d, 2 P, J_{pp} = 13 Hz), –59.7 (t, 1 P).

Preparation of [2,2-Di(methyl-d_3)propyl]tris(trimethylphosphine)iridium(I) (1-d_6). 1-Lithio-2,2-di(methyl-d_3)propane was prepared as outlined previously.[16] This was used to prepare 1-d_6 in a manner completely analogous to that for 1 above. The ${}^{31}P\{{}^1H\}$NMR spectrum was identical with that of 1.

Preparation of [(Trimethylsilyl)methyl]tris(trimethylphosphine)iridium(I) (2) and Its Cyclization to (η^2-2,2-Dimethyl-2-silatrimethylene)hydridotris(trimethylphosphine)iridium(III) (4). Pentane (45 mL) was added to a Schlenk flask containing 508 mg (0.95 mmol) of $[L_4Ir]Cl$ and 90 mg (0.95 mmol) of ((trimethylsilyl)methyl)lithium in an acetone/dry ice bath. The flask was moved to an ice/salt bath, and the heterogeneous mixture was stirred under argon for 6 h with the temperature maintained between –17 and –15 °C. The mixture was filtered through Celite with use of a jacketed fritted filter surrounded by a –78 °C bath. The orange solution was reduced to a small volume in an ice bath and was allowed to crystallize at –20 °C. The solid was washed twice at –78 °C with 0.5 mL of pentane, dried under vacuum, and stored at –20 °C. The material is labile and must be stored cold. The ${}^1H$ NMR spectrum of 2 agrees well with that published.[6] ${}^{31}P\{{}^1H\}$ NMR (pentane): δ –24.3 (d, 2 P, J_{pp} = 20 Hz), –31.2 (t, 1 P).

Complex 2 was cyclometalated by heating at 55 °C in pentane solution for several hours. The reaction was quantitative by NMR spectroscopy. The ${}^1H$ and ${}^{31}P\{{}^1H\}$ NMR spectra of 4 agreed well with those published.[6] ${}^{31}P\{{}^1H\}$ NMR (pentane): δ 57.4 (d, 2 P, J_{pp} = 13 Hz), –59.8 (t, 1 P).

Prepartion of [(Methyldi(methyl-d_3)silyl)methyl]tris(trimethylphosphine)iridium(I) (2-d_6). ((Methyldi(methyl-d_3)silyl)methyl)lithium was prepared as outlined previously.[16] This was used to prepare 2-d_6 in a manner completely analogous to

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that for **2** above. The $^{31}P\{^1H\}$ NMR spectrum was identical with that of **2**.

Preparation of [(Tri(methyl-d_3)silyl)methyl]tris(trimethylphosphine)iridium(I) (2-d_9). $(CD_3)_3SiCH_2Cl$ was prepared by standard procedures from freshly distilled commercial Cl_3SiCH_2Cl and 3 equiv of CD_3MgI with use of ether solvent, giving a 40% yield of pure material (GLPC), bp 94–96 °C. This chloride was used to prepare the lithium reagent, again with use of standard procedures, from lithium metal containing ca. 2% sodium in pentane under argon. The solvent was removed, and the lithium reagent was stored as a solid (98% yield). The same procedure as above was used to prepare 2-d_9 from 343 mg of $[L_4Ir]Cl$ and 67 mg of $(CD_3)_3SiCH_2Li$. The $^{31}P\{^1H\}$ NMR spectrum was identical with that of **2**.

Kinetics of Cyclometalation: Activation Parameters. Pentane solutions of **1** or **2** in sealed NMR tubes were prepared as described above and stored at −78 °C. Each sample was in turn placed in the temperarture-equilibrated probe of the NMR spectrometer, the sample was allowed to equilibrate, and the rate of the reaction was followed by monitoring the $^{31}P\{^1H\}$ resonances with continuous data acquisition. The rate constants and their standard errors are listed in Table I. Standard Arrhenius treatment gave the activation parameters and standard errors in Table II.

Kinetics of Cyclometalation with Free L. To samples of **1** or **2** in pentane prepared as described above were added small amounts of trimethylphosphine before sealing. NMR integration indicated the concentrations of L and **1** or **2**. The rates of cyclometalation were followed by continuous $^{31}P\{^1H\}$ data acquisition in the probe of an NMR spectrometer at the specified temperature. The calculated rate constants, temperatures, and L concentrations are shown in Table I.

Cyclometalation of 1 or 2 with Free L/L′. The following example is given for **1**. Pentane solvent and ca. 5 mmol of a 1/2.5 mixture of L/L′ were distilled into a sample tube equipped with a magnetic stirbar and containing 50 mg (0.094 mmol) of $[L_4Os]Cl$ and 9 mg (0.12 mmol) of neopentyllithium, and the tube was sealed. This sample was stirred at −20 °C for 5 h and then at room temperature for several hours. Volatiles were removed under vacuum, the solid was extracted with pentane, and this solution was sealed in an NMR tube. The $^{31}P\{^1H\}$ NMR spectrum of the resulting 3-d_0, 3-d_9, 3-d_{18}, and 3-d_{27} mixture is shown in Figure 2a. Resonances for coordinated $P(CH_3)_3$ ligands appeared at δ −59.1 (d) and −59.7 (t), while those of $P(CD_3)_3$ appeared at δ −61.2 and −61.7 (t). The three resonances at higher field were broad, but the doublet at δ −59.1 was superimposed by a pair of doublets resulting from the cis L and L′ coupling of the isomers 3-d_9(e) and 3-d_{18}(g) (see Figure 1). J_{pp} for this new doublet component is 4.2 Hz, and the half-height width of the lowest field peak and its flanking doublet all together is 7.3 Hz (Figure 2a).

Complex **2** was prepared in situ in the presence of L/L′ in the same way as described for **1**. The resulting $^{31}P\{^1H\}$ NMR spectrum of the 4-d_0, 4-d_9, 4-d_{18}, and 4-d_{27} mixture showed Ir–$P(CH_3)_3$ resonances at δ −57.4 and −59.8 and Ir–$P(CD_3)_3$ resonances at δ −59.3 and −61.8. The δ −57.4 peak showed cis L/L′ coupling, but it was not well-resolved.

Kinetics of Exchange of 3 with L′. The product from several cyclometalations of **1** was combined and was recrystallized from hot hexane. The colorless crystalline **3** was washed with cold hexane and dried under vacuum. A 20.7-mg sample of this material was sealed in an NMR tube along with benzene solvent and a moderate amount of L′. $^{31}P\{^1H\}$ NMR spectra revealed the sample to be ca. 0.005 M in **3** and 2.4 M in L′. The sample was heated in the temperature-equilibrated probe of an NMR spectrometer at 95 °C, and the rate of exchange was monitored by continuous acquisiton of $^{31}P\{^1H\}$ data. The resonances at δ −59.1 and −59.7 disappeared, and new ones appeared at δ −6.12 and −61.7 both in a cleanly first-order manner. A spectrum for this exchange at ca. two-thirds reaction is shown in Figure 2b. The resonance at δ −59.1 remained a sharp doublet throughout; no additional splitting was visible. The rate constant is $(4.13 \ (0.52)) \times 10^{-5}$ s^{-1}.

Kinetics of Exchange of 4 with L′. The product **4** from several cyclometalations of **2** was combined and recrystallized, as described for **3** above, yielding colorless crystalline **4**. A 12.8-mg sample of this material was sealed in an NMR tube along with benzene solvent and a small amount of L′. $^{31}P\{^1H\}$ NMR spectra revealed the sample to be ca. 0.004 M in **4** and 0.25 M in L′. The sample was heated in the temperature-equilibrated probe of an NMR spectrometer at 95 °C, and the rate of exchange was monitored by continuous acquisition of $^{31}P\{^1H\}$ data. The resonances at δ −57.4 and −59.8 disappeared, and new ones appeared at δ −59.3 and −61.8, both in a cleanly first-order manner. No hint of splitting of the δ −57.4 resonance was detectable. The rate constant is $(2.54 \ (0.14)) \times 10^{-5}$ s^{-1}.