Ligand Exchange Reactions of Iridium Hydrido Formyl Compounds†

David L. Thorn* and D. C. Roe

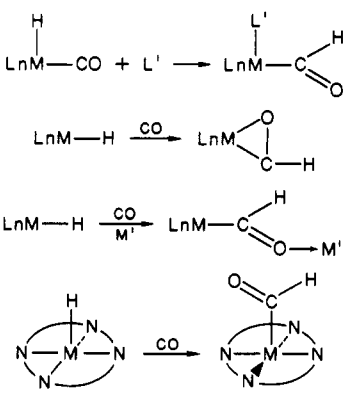
E. I. du Pont de Nemours and Company, Central Research and Development Department, Experimental Station, Wilmington, Delaware 19898

Received June 20, 1986

Facile halide, CO, and PMe_3 substitution for the iodide ligand of $IrH(CHO)I(PMe_3)_3$ (**1a**) has been observed. The evidence supports a conventional dissociative mechanism for the substitution reaction: an acetonitrile-solvated 16-electron hydrido formyl compound has been detected following treatment of compound **1a** with silver ion, and mechanisms involving mobile hydrogen atoms have been ruled out by isotope labeling studies.

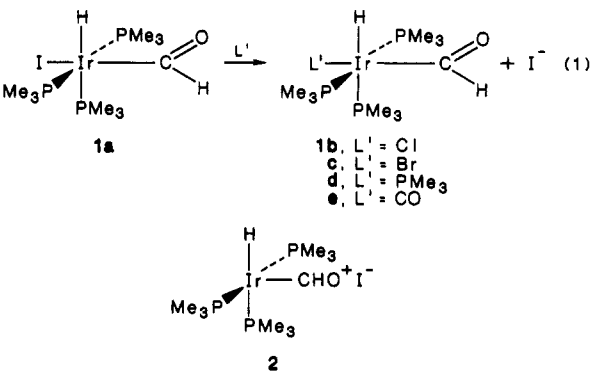
Introduction

Formyl compounds of the transition metals have been the subject of active investigation, as they may be key intermediates in the reduction of carbon monoxide and formation of organic products. While a substantial number of stable formyl complexes are known at this time,[1] only one has been reported to be prepared by the presumably straightforward transformation of a hydrido carbonyl compound illustrated in reaction A.[2] There are several other fascinating and potentially useful syntheses of formyl compounds from hydrido compounds and CO or carbonyl compounds, but in each case there is an important exception to the mechanism of reaction A, either a strong component of direct intramolecular M–O interaction (reaction B),[3] or intermolecular M–O interaction (reaction C),[4] or a ligand environment that precludes a stable cis hydrido carbonyl structure (reaction D).[5]



The general inability to prepare stable formyl compounds by reaction A is a puzzling contrast to the often-facile "CO insertion" reaction of analogous alkyl compounds. Consideration of the thermodynamic parameters of the species of reaction A has led to the claim that the forward reaction of (A) will usually be endothermic and that the reverse of this reaction, formyl decomposition to hydrido carbonyl compounds, will be favored, subject to the exceptions noted above.[1,6] Consistent with this claim, the formyl compounds that have been studied in this laboratory do decompose according to the reverse reaction of (A), given the appropriate conditions.[7] "Appropriate conditions" here means opening a coordination site at the metal center to make room for the hydrogen atom. In fact, we and other workers have assumed that kinetically stable formyl compounds require metal complexes with tightly bound supporting ligands, as ligand dissociation could allow formyl decomposition in the reverse reaction of (A).[1,6,8,9]

Therefore, it was with great surprise that we discovered the rapid, stereospecific, and high-yield ligand exchange reaction of formyl compound **1a** summarized in eq 1.



† Contribution No. 4089.

(1) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1–38. For references to stable formyl compounds reported after publication of this review article, see: Smith, G.; Cole-Hamilton, D. J.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 2501–2507. Berke, H.; Huttner, G.; Scheidsteger, O.; Weiler, G. *Angew. Chem.* **1984**, *96*, 693; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 735–736. Lilga, M. A.; Ibers, J. A. *Organometallics* **1985**, *4*, 590–598.

(2) Floriani, C. *Pure Appl. Chem.* **1983**, *55*, 1–10.

(3) Fagan, P. J.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6959–6962. Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051–7064.

(4) Many researchers have studied the remarkable reactions between early-transition-metal hydrido and carbonyl compounds (or CO) but in only a few cases have recognizable metalloformyl products been isolated: Wolczanski, P. T.; Threlkel, R. S.; Santarsiero, B. D. *Acta Crystalogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 1330–1333. Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121–127 and references therein. Belmonte, P. A.; Cloke, F. G. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 2643–2650. Churchill, M. R.; Wasserman, H. J. *J. Chem. Soc., Chem. Commun.* **1981**, 274–275.

(5) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 700–701. Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302–303. Wayland, B. B.; Duttaahmed, A.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1983**, 142–143.

(6) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238–244. Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Jones, W. D.; Harsy, S. G. *J. Mol. Catal.* **1981**, *13*, 43–59.

(7) Thorn, D. L. *Organometallics* **1982**, *1*, 197–204.

(8) Smith, G.; Cole-Hamilton, D. J. *J. Chem. Soc., Dalton Trans.* **1984**, 1203–1208. Smith, G.; Sutcliffe, L. H.; Cole-Hamilton, D. J. *Ibid.* **1984**, 1209–1214.

(9) In addition to facile intramolecular decomposition by this mechanism, several other pathways are known for decomposition of formyl compounds, including homolytic fission, intermolecular hydride transfer, and hydrogen atom transfer. See ref 1. See also: Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141–152. Narayanan, B. A.; Amatore, C.; Casey, C. P.; Kochi, J. K. *Ibid.* **1983**, *105*, 6351–6352. Sumner, C. E.; Nelson, G. O. *Ibid.* **1984**, 106, 432–433. Barratt, D. S.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1985**, 458–459. Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1986**, *5*, 926–935.

0276-7333/87/2306-0617$01.50/0

Table I. ^{1}H NMR Spectra[a] of Hydrido Formyl Compounds

compound[b]	^{1}H NMR		
	hydride	formyl	PMe_3
$IrH(CHO)I(PMe_3)_3$ (**1a**)	−10.6 [d ($J_{H-P_{trans}}$ = 138) of ($J_{H-P_{cis}}$ = 19.5) of m]	14.62 [t ($J_{H-P_{cis}}$ = 6.6) of d (3.6) of d (2.2)]	1.60 [d (8.3) of d ($J_{H-H-hydride}$ = 0.8)] 1.74 [t (3.7)]
$IrH(CHO)Cl(PMe_3)_3$ (**1b**)	−9.8 [d (139) of t (20) of m]	14.65 [t (6.7) of t (2.4)]	1.47 [d (8.5) of d (0.9)] 1.59 [t (3.8)]
$IrH(CHO)Br(PMe_3)_3$ (**1c**)	−10.0 [d (138) of t (20) of m]	14.58 [t (6.5) of d (3.0) of d (2.2)]	1.51 [d (8.5) of d (0.8)] 1.65 [t (3.8)]
$IrH(CHO)(PMe_3)_4^+I^-$ (**1d**)	−12.05 [d (125) of quartets (19) of m]	15.08 [d (48) of quartets (5.5) of d (1.8)]	1.60 [d (7.9)] 1.62 [d (8.0) of d (0.9)] 1.63 [t (3.7)]
$IrH(CHO)(CO)(PMe_3)_3^+I^-$ (**1e**)	−10.4 [d (111) of t (18) of m]	14.65 [t (8.0) of d (3.8) of d (3.0)]	1.70 [d (9.0)] 1.80 [t (4.0)]
$IrH(CHO)(CD_3CN)(PMe_3)_3^+SbF_6^-$	−10.3 [d (128) of t (20) of m]	14.26 [t (7.8) of t (2.4)]	1.53 [d (8.4) of d (0.8)] 1.64 [t (3.8)]
fac-$IrH_2(CO)(PMe_3)_3^+SbF_6^-$	−11.9 [d (94) of m (pseudo d, 23)]		1.77 [d (9.1), integral 18] 1.79 [d (10.8), integral 9]
mer-$IrH_2(CO)(PMe_3)_3^+SbF_6^-$	−10.9 [t ($J_{H-P_{cis}}$ = 1.96) of d ($J_{H-P_{cis}}$ = 16.5) of d (J_{H-H} = 4.3)] −11.6 [d ($J_{H-P_{trans}}$ = 113.7) of t ($J_{H-P_{cis}}$ = 20.1) of d (J_{H-H} = 4.3)]		1.76 [d (9.4) of d ($J_{H-hydride}$ = 0.8)] 1.82 [t (4.1)]
$IrD(CHO)Cl(PMe_3)_3$ (**4**)		14.66 [t (6.7) of d (2.2)]	1.48 [d (8.5)] 1.60 [t (3.9)]
$IrD(CHO)(PMe_3)_4^+Cl^-$		15.08 [d (48) of quartets (5.9)]	1.62 [m]

[a] Measured in CD_3CN solution at ambient probe temperature. Chemical shifts in parts per million downfield from external Me_4Si. (Solvent at 1.95 ppm.) Coupling constants in parentheses in hertz. [b] All hydrido formyl compounds have the *cis,mer* structure indicated in the equations.

Ligand exchange on octahedral d^6 compounds usually proceeds by a dissociative mechanism; thus the coordinatively unsaturated formyl compound **2** could be a kinetically accessible species, stable with respect to decomposition of the formyl group. Described in this paper are the ligand exchange reactions, some studies that support a dissociative mechanism involving compound **2**, and some implications of these observations.

Results and Discussion

The Exchange Reaction. The initial observation was that the iodo hydrido formyl compound **1a**[10] in pyridine solution with a soluble alkylpyridinium bromide salt equilibrated with the bromo hydrido formyl compound. Subsequently it was found that chloride, CO, and PMe_3 also would substitute for iodide in acetonitrile solution and PMe_3 would substitute for chloride in the chlorohydridoformyl compound **1b**. The halide substitution reactions occurred readily at room temperature in acetonitrile solution, and equilibrium was established within 5 min. The PMe_3 substitution reaction was slower ($t_{1/2} \simeq 13$ min: see Experimental Section) but went to completion with no measurable concentration of halo formyl complex remaining. The CO substitution reaction was much slower (hours at 1 atm in acetonitrile). In each case the product has been identified by its ^{1}H NMR spectrum, that of the chloride- and PMe_3-substituted products **1b** and **1d**, respectively, being identical with the spectrum of an authentic sample prepared by other routes.[7] The halide and PMe_3 substitutions occur in good yield with no detectable formyl decomposition. The CO substitution reactions show decomposition products, mainly *fac*- and *mer*-$IrH_2(CO)(PMe_3)_3^+$, whose amounts vary from sample to sample, which suggests some effect of trace impurities.

The substitution reactions occur most rapidly in polar solvents (acetonitrile, pyridine) and much less rapidly in less polar solvents (benzene, tetrahydrofuran), which is consistent with halide dissociation being an important step. Even stronger evidence for halide dissociation is that a new hydrido formyl compound, presumably $IrH(CHO)(PMe_3)_3(CD_3CN)^+SbF_6^-$, is formed rapidly (detected by ^{1}H NMR after the silver halide is removed) when a CD_3CN solution of iodo compound **1a** (or its chloro analogue **1b**) is treated with an equivalent of $AgSbF_6$. In solution this proposed acetonitrile formyl compound reacts rapidly with added ligand to make the stable formyl derivatives; its reaction with CO proceeds much more rapidly than the reaction between **1a** and CO, again consistent with slow halide loss from **1a** being a crucial step. However, on standing or on attempted isolation this proposed acetonitrile formyl compound decomposes to $IrH_2(CO)(PMe_3)_3^+SbF_6^-$. Interestingly, the dihydridocarbonyltris(trimethylphosphine)iridium(III) cation formed from this decomposition initially has the *fac* geometry, but this *fac* isomer readily rearranges to the more stable *mer* isomer reported earlier.[7]

Despite this evidence for a dissociative mechanism, there are attractive alternatives that do not involve compound **2**. Perhaps the most attractive alternative is the associative mechanism of eq 2, where the η^1-formaldehyde complex **3** is the key species.[11] As the η^1-formaldehyde group can be viewed as a deprotonated hydroxymethyl group and iridium hydroxymethyl compounds are known[10,12] (one even formed by a hydrogen migration reaction very similar to that implicit in eq 2[12,13]), it is necessary to provide convincing evidence against the mechanism of eq 2 before eq 1 can be comfortably accepted. Isotopic labeling was

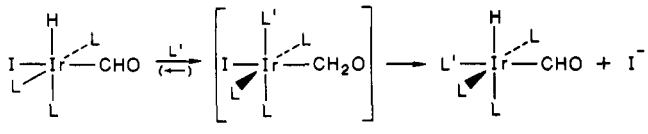
(10) Thorn, D. L.; Tulip, T. H. *Organometallics* **1982**, *1*, 1580–1586.

(11) Nonbridging η^1-formaldehyde adducts have not been observed, but several η^2-formaldehyde adducts have been isolated, following the initial report by: Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503–505. See, for example: Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Ibid.* **1985**, *107*, 2985–2986 and references therein.

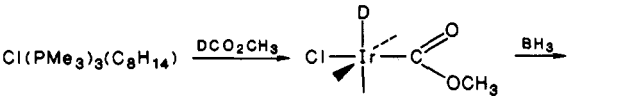
(12) Thorn, D. L.; Calabrese, J. C. *J. Organomet. Chem.* **1984**, *272*, 283–293.

(13) Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1982**, *231*, 335–360.

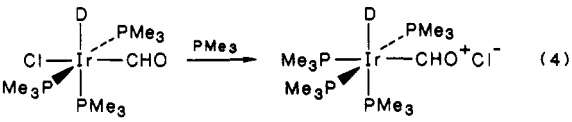
chosen as a means of exploring the possible mechanism summarized in eq 2. The specifically labeled compound **4** was synthesized by the reactions of eq 3 and its isotopic



1a **3**, L = PMe_3 (2)



4 (3)

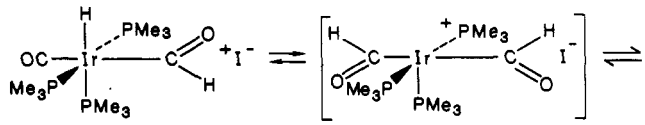


4 (4)

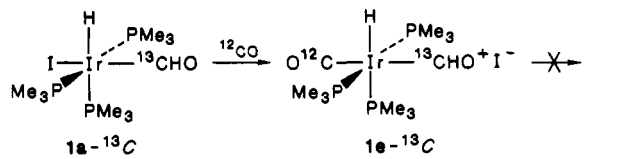
purity confirmed by ^1H NMR. The exchange reaction with PMe_3 yielded exclusively the labeled product shown in Eq 4. The retention of the deuterium on the metal throughout the substitution reaction is compelling evidence against the mechanism of eq 2 because the hydrogen atoms of the η^1-formaldehyde intermediates **3** are equivalent and H–D scrambling would have occurred in the deuterium-labeled material. Note in passing that the observed deuterido formyl product of eq 4 is thermodynamically less stable than its isotopically permuted isomer, the hydrido deuterioformyl compound.[14] It is inconceivable that the less stable isotopic isomer would be formed exclusively if there were any actual opportunity for scrambling. Thus we confidently rule out compound **3** (and other CH_2O-containing species) as a reaction participant and discard any hypothetical mechanism (e.g. eq 2) that requires it.

Hydrogen Atom Mobility: Comments. The probable intermediate compound **2** owes at least some of its stability to its apparent rigidity: any other isomer has a vacant coordination site directly adjacent to the formyl group, and decomposition to the dihydrido carbonyl tris(phosphine) complex should be rapid. Rigid pentacoordinate, 16-electron complexes of d^6 metals are known as substitution intermediates and even as isolated species, perhaps most relevant being pentacoordinate Rh(III) acyl compounds[15] and even (porphyrin)rhodium(III) formyl compounds.[5] Thus rigidity of compound **2** is not without precedent, although hydrido compounds are more prone to rearrangements than most compounds. In any case, if compound **2** is indeed rigid during the time of its existence—which is very brief—the stability of the formyl group is easily understood. However, Lilga and Ibers[1] observed that the formyl compound *cis*-$(diphos)_2IrCl(CHO)^+$ can rearrange, possibly following reversible dechelation of the diphos ligand, so the stability of the iridium formyl group need not depend entirely upon coordination rigidity.

A second aspect of hydrogen atom mobility can be explored with the new compound **1e**, as outlined in eq 5. Here the hydrido hydrogen atom could move to the carbonyl ligand to make a new formyl group while the original formyl group decomposes to hydrido and carbonyl ligands. As the product is degenerate with the reactant, we thought this reaction might provide an example of the hydrido carbonyl-to-formyl process proposed for rapid substitution reactions of certain hydrido compounds.[16] However, a second labeling study (eq 6) ruled this out, there being no



1e (5)



1a-^{13}C **1e**-^{13}C (6)

detectable interconversion of ^{12}C and ^{13}C formyl groups during the solution lifetime of compound **1e** (up to several days at room temperature). An attempt to force this interconversion by heating a sample of compound **1e**-^{13}CHO under ^{12}CO pressure failed, and only decomposition products were detected. These observations are consistent with the above discussion of reaction A: conversion of the hydrido and carbonyl ligands to a formyl group is unobservably slow, even though any necessary thermodynamic driving force could be provided by the near-simultaneous decomposition of the [^{13}C]formyl group to hydrido and ^{13}CO ligands.

Summary and Conclusions

Substitution reactions require labile ligands and accessible coordination sites, but compounds that have them cannot normally support a stable formyl group, owing to rapid and irreversible formyl decomposition by the reverse reaction of (A). But hydrido formyl iridium compounds do exhibit substitution reactivity, apparently by conventional dissociative mechanisms. Reasons why ligand dissociation does not result in formyl decomposition in this iridium system are not known, but one contributing factor is the apparent rigidity of the 16-electron species **2**.

Experimental Section

Compounds **1a**[10] and **1b,d**[7] were prepared according to published methods. The deuterido formyl compound **4** was prepared by borane reduction of the deuterido methoxycarbonyl compound,

(14) A zero-point energy calculation using 2072 cm^{-1} for the Ir–H stretching frequency and 2622 cm^{-1} for the C–H stretching frequency of $IrH(CHO)(PMe_3)_4^+$ (see ref 7), and calculated values for the corresponding deuterio stretching frequencies, results in the observed isomer $[IrD(CHO)(PMe_3)_4]^+$ being 45 cm^{-1} or 0.13 kcal/mol less stable than its isotopically permuted isomer $[IrH(CDO)(PMe_3)_4]^+$.

(15) Structurally characterized pentacoordinate acylrhodium(III) compounds include those reported by: Egglestone, D. L.; Baird, M. C.; Lock, C. J. L.; Turner, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1576–1582. Cheng, C.-H.; Spivack, B. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1977**, *99*, 3003–3011. Lau, K. S. Y.; Becker, Y.; Huang, F.; Baenziger, N.; Stille, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 5664–5672. Cheng, C. H.; Eisenberg, R. *Inorg. Chem.* **1979**, *18*, 1418–1424. McGuiggan, M. F.; Doughty, D. H.; Pignolet, L. H. *J. Organomet. Chem.* **1980**, *185*, 241–249. Bennett, M. A.; Jeffery, J. C.; Robertson, G. B. *Inorg. Chem.* **1981**, *20*, 323–330. Grigg, R.; Trocha-Grimshaw, J.; Henrick, K. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 2455–2458.

(16) Pearson, R. G.; Walker, H. W.; Mauermann, H.; Ford, P. C. *Inorg. Chem.* **1981**, *20*, 2741–2743.

which in turn was prepared by reacting methyl formate-*d* with chlorotris(trimethylphosphine)(cyclooctene)iridium(I).[7] NMR spectra were recorded at ambient probe temperature by using a Nicolet/GE QE-300 instrument. ^{1}H NMR spectra for all compounds are reported in Table I.

In a typical exchange reaction, compound **1a** (0.03 g) in CD_3CN solution was treated with 2 equiv of Ph_4AsCl. The NMR spectrum, run within 30 min of mixing, showed 85% conversion of the iodo formyl compound **1a** to the known[7] chloro formyl compound **1b**, with no decomposition products detectable. Addition of further amounts of Ph_4AsCl drove the reaction essentially to completion. The ^{1}H NMR spectrum of the reaction solution was identical (hydride, formyl, $P(CH_3)_3$) with the ^{1}H NMR spectrum of an authentic sample of compound **1b** prepared by the literature route.[7] The equilibrium constant for the reaction **1a** + $(C_6H_5)_4AsCl \rightleftharpoons$ **1b** + $(C_6H_5)_4AsI$ is 4.1 ± 0.1 at 20 °C in CD_3CN.

For a quantitative determination of the rate of PMe_3 exchange, the ^{1}H NMR spectrum of a CD_3CN solution of compound **1a** (initially 0.087 M) and PMe_3 (initially 0.173 M) was monitored. The pseudo-first-order rate constant for the reaction **1a** → **1d** was 0.053 ± 0.001 min^{-1}; $t_{1/2}$ = 13 min at 20 °C.

In our attempt to force the ^{12}C–^{13}C interconversion of compound **1e**-^{13}*C*, a sapphire NMR tube[17] containing [^{13}*C*]formyl compound **1a**-^{13}C in CD_3CN was pressurized to 25 atm with ^{12}CO. After 24 h at room temperature the solution contained approximately equal amounts of compound **1e**-^{13}*CHO* and *mer*-$[IrH_2(^{13}CO)(PMe_3)_3]I$. No **1e**-^{12}*CHO* could be detected. The NMR tube was then heated to 80 °C. After 24 h *mer*-$[IrH_2(^{12}CO)(PMe_3)_3]I$ was the only detectable compound present.

(17) Roe, D. C. *J. Magn. Reson.* **1985**, *63*, 388–391.

Ligand Effects and Nucleophilic Addition to (η^3-Allyl)palladium Complexes. A Carbon-13 Nuclear Magnetic Resonance Study[1]

Björn Åkermark,* Bertil Krakenberger, and Sverker Hansson

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Aldo Vitagliano*

Dipartimento di Chimica, Università di Napoli, 80134 Napoli, Italy

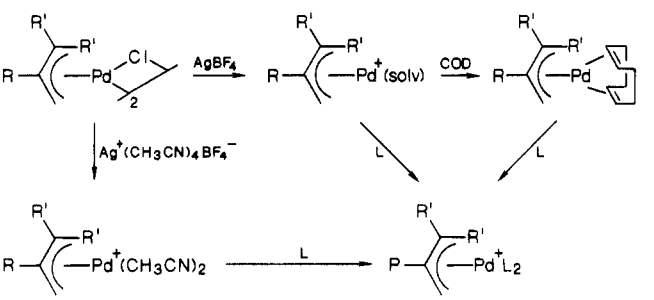
Received April 9, 1986

With the use of acceptor ligands such as phosphines, large downfield ^{13}C shifts may be induced selectively at the more substituted terminus of an unsymmetric (η^3-allyl)palladium system. Bidentate ligands with one acceptor and one donor function may induce even greater relative downfield shifts at the more substituted terminus. The observed downfield chemical shifts follow closely the anticipated acceptor properties of the ligands, suggesting that there may be a relation between ^{13}C NMR shifts and relative charge at the η^3-allyl termini.

Nucleophilic addition to η^3-allyl systems has been extensively applied to selective organic synthesis, in particular after the development by Trost and associates of catalytic reactions starting with allylic acetates.[2] One important problem with these reactions is to control the regiochemistry. For instance, the reaction of **64** (L^1 = PPh_3, L^2 = Cl^-) with the anion of dimethyl malonate gives a mixture of the two possible regioisomers. However, when more sterically demanding nucleophiles such as the anion of benzenesulfonyl acetate are used,[2c] the less substituted terminus of the η^3-allyl system reacts preferentially.

In a recent study of the reactions of (η^3-geranyl)palladium complexes, it was observed that ligands such as triphenylphosphine induced reactivity at the more substituted η^3-allyl terminus[3] while bipyridine promoted reaction at the less substituted terminus.[3a] This result can be interpreted as a correlation between acceptor properties of the ligands and relative reactivity at the more substituted η^3-allyl terminus. Selective reaction at the more substituted η^3-allyl terminus has been observed before[2c,4,5] but explained in terms of relative stability of the products[2c,4a] or by the intermediacy of a σ-complex.[5] However, another explanation is that acceptor ligands such as triphenylphosphine selectively induce positive charge at the more substituted η^3-allyl terminus. In fact, Trost and his associates have recently presented results from molybde-

Scheme I



(1) Presented in part at XIIth International Conference on Organometallic Chemistry, Vienna, 1985.

(2) (a) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (b) Trost, B. M.; Verhoeven, T. R. *Compr. Organomet. Chem.* **1982**, *8*, 799. (c) Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4730.

(3) (a) Åkermark, B.; Vitagliano, A. *Organometallics*, **1985**, *4*, 1275. (b) Åkermark, B.; Hansson, S.; Krakenberger, B.; Vitagliano, A.; Zetterberg, K. *Organometallics* **1984**, *3*, 679.

(4) (a) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416. (b) Adams, R. D.; Chodosh, D. F.; Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 2570.

(5) Takahashi, U.; Tsukiyama, K.; Sakai, S.; Ishii, Y. *Tetrahedron Lett.* **1970**, 1913.

0276-7333/87/2306-0620$01.50/0