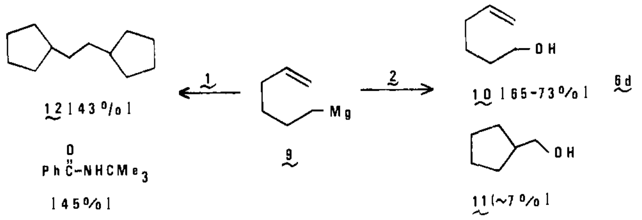

dimethyl peroxide.[20] Miller has argued that the reaction of Grignard and lithium reagents with *o*-quinol acetates to afford ethers occurs by an initial electron transfer (ET) between the organometallic reagent and the *o*-quinol acetate followed by combination of phenoxy and alkyl radicals.[21]

To ascertain whether or not ET mechanisms could account for the hydroxylation and coupling of R′M by oxaziridines (Scheme I) we explored the reactions of **1** and **2** with 5-hexenylmagnesium bromide (**9**).[19,22] Compound **9**, has proven useful for detecting radical intermediates because of the extremely rapid cyclization ($K_{\text{cycl}} = 10^5$ s) of the 5-hexenyl radical to the cyclopentyl methyl radical.[21] Addition of **2** to a 3-fold excess of **9** in ether affords on workup (vide supra) a 65–73% yield of 1-hexen-6-ol (**10**) and ~7% cyclopentylmethanol (**11**).[23] The adduct **6d** was isolated by preparative TLC (silica gel) in 54% yield.[12] The isolation of alcohol **10** in good yield is consistent with the mechanism outlined in Scheme II. If ET had been important, **11** would have been formed in much higher yield.[19] The low yield of **11** undoubtedly occurs by reaction of cyclopentylmethylmagnesium bromide, formed in the preparation of **9**, with the oxaziridine. Similar observations have been reported by others.[22,24]

In contrast to **2**, oxaziridine **1** reacts with **9** to afford a 43% yield of 1,2-dicyclopentylethane (**12**)[25] and a 45% yield of *N*-*tert*-butylbenzamide.[24,26] ET from R′M to the oxaziridine followed by combination of radical or radical-like intermediates is consistent with these results. The fact that **1** and *n*-octylmagnesium bromide (Table I, entry 2) gave a high yield of hexadecane without any detectable amounts of 1-octene, the disproportionation product, suggests that the coupling reaction (pathway A) involves caged rather than "free" radical species. Coupling of organometallic reagents by various transition metals is well known.[27] These reactions are generally not considered to involve "free" radicals but are believed to be of a bimolecular nature.

The difference in reactivity exemplified by oxaziridines **1** and **2** with organometallic reagents can best be ascribed to the presence of the powerful electron-attracting sulfonyl group which increases the electrophilicity of the oxaziridine oxygen atom and may inhibit ET from R′M to the oxaziridine. Although lithium reagents are reportedly better at transferring an electron than Grignard reagents,[28] the former compounds are much harder nucleophiles than the latter reagents. Perhaps the simplest explanation for the hydroxylation of phenyllithium by **1** and not by *n*-butyllithium (Table I, entries 3 and 4) can be ascribed to the differences in stability between phenyl and *n*-butyl radicals.[29]

Studies aimed at exploring the scope of the reaction of organometallic reagents with oxaziridines are currently in progress.

Acknowledgment. This investigation was supported by Public Health Service Grant No. CA 14341 from the National Cancer Institute, Department of Health, Education and Welfare.

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(12) All new compound had satisfactory elemental analysis and had IR and NMR spectra consistent with the proposed structures: **5a**, mp 51–52 °, **5c**, bp 60 °C (0.1 mm); **6b**, mp 72–73 °C, **6c**, 71–72 °C; **6d**, 42–43 °C.
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(26) Several minor compounds that were not characterized were detected by GLC. These same compounds are observed in blank solutions of **9**. See also ref 23.
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Transition Metal Activation of Aldehydes: Platinum Metal Derivatives of *o*-Diphenylphosphinobenzaldehyde

Sir:

The reactivity of aldehydes toward metal ions remains an obscure area of coordination chemistry despite the widespread dependence of the preparations and reactions of the formyl group on metal ion catalysis in industrial synthesis where aldehydes are prepared via palladium catalyzed oxidation and the cobalt and rhodium catalyzed hydroformylation of olefins.[1] Hydrogenations,[2] hydrosilylations,[3] and decarbonylations[4] of the formyl group proceed via platinum metals catalysis; additionally, the hydroacylation of olefins is promoted by rhodium[5] and ruthenium[7] compounds. The prevailing interest in the transition metal induced scission and formation of C–H and C–C bonds[8] renders our synthetic and mechanistic results on these processes especially timely. We find that *o*-diphenylphosphinobenzaldehyde[9] (**1**, abbreviated PCHO) stabilizes intermediates in the reactions of the aldehyde group with

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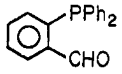
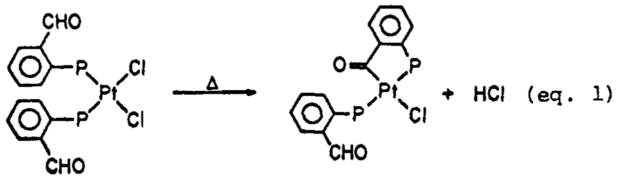


several metal ions which reveal new mechanistic information concerning metal–hydrocarbon interactions.

Vacuum thermolysis (250 °C) of *cis*-PtCl$_2$(PCHO)$_2$ (**2**), which is easily prepared from **1** (2 equiv) and K$_2$PtCl$_4$ and contains only monodentate P-bound phosphines,[10] results in rapid and quantitative formation of the bright yellow air-stable acyl complex PtCl(PCHO–H)(PCHO) (**3**).[11] This reaction is accompanied by the evolution of HCl which was trapped and titrated (eq 1, unsubstituted Ph groups omitted for clarity). This is the first reported preparation of a metal acyl by intramolecular elimination of HCl from a metal–aldehyde complex.



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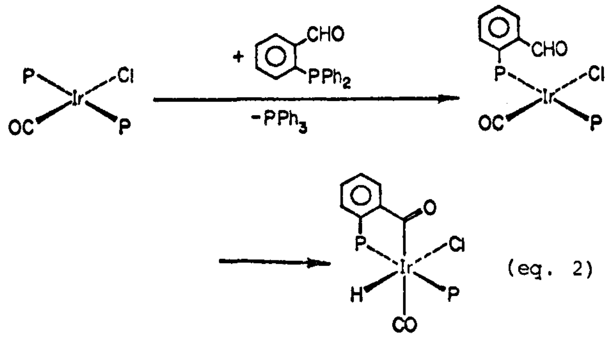
3

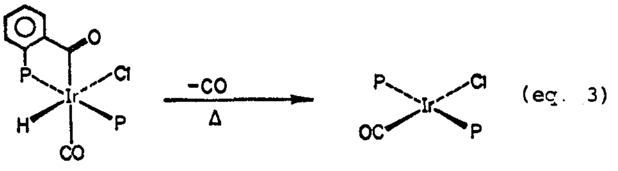
One can envision this reaction as proceeding via two distinct pathways: oxidative addition of the C–H bond followed by reductive elimination of HCl, or direct electrophilic attack on the formyl group by platinum(II) with displacement of a proton.[12]

In contrast to the platinum(II) reaction, treatment of **1** with nucleophilic iridium(I) complexes results in oxidative addition affording hydrides. For example, reaction of *trans*-IrCl(CO)(PPh$_3$)$_2$ with **1** (1 mol) in benzene at room temperature cleanly yields the iridium(III) acyl hydride IrCl(PCHO-H)CO(H)(PPh$_3$) (**4**), which was isolated as pale yellow crystals upon addition of hexane (eq 2).[13] ^{1}H and ^{31}P NMR data for **4** require the phosphines to be mutually trans and cis



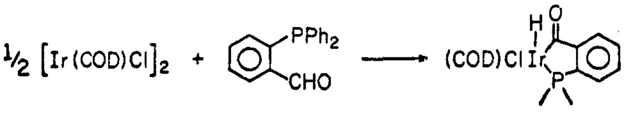
4

to the hydride; assuming cis oxidative addition, only the relative stereochemistry of the Cl and CO ligands remains uncertain. Compound **4** decarbonylates in refluxing xylene (bp 139–141 °C) in 1 h to afford the starting complex in high yield, eq 3, wherein one triphenylphosphine ligand is now derived from **1**.



The overall process of oxidative addition of the aldehyde and reductive elimination of the arene confirms the previously suggested mechanism of aldehyde decarbonylation.[14]

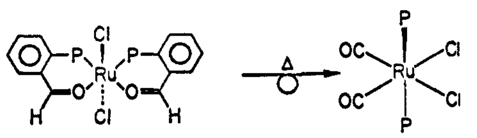
The reaction of **1** with 0.5 equiv of [IrCl(COD)]$_2$ (COD = 1,5-cyclooctadiene) proceeds via bridge cleavage–oxidative addition to afford the thermally unstable acyl hydrido olefin complex, IrCl(PCHO–H)H(COD) (**5**).[15] The lability of **5** precluded its purification; however, the complex was definitively characterized spectroscopically. ^{1}H NMR spectroscopy for **5** shows absorbances for the aromatic, coordinated olefinic, alkyl and hydridic hydrogens, and the latter is coupled to one phosphorus (J_{PH} = 15 Hz). The infrared spectrum of **5** shows absorptions for the hydride and the acyl in positions very similar to those found for **4**.[15] Compound **5** is a unique example of a metal complex containing both coordinated aldehyde fragments and olefin, and as such represents a model for an intermediate in the metal catalyzed hydroacylation of olefins.



5

(eq. 4)

While the reactions of **1** with platinum(II) and iridium(I) are two possible routes available for aldehyde activation by metal ions, it is clear from the results below that other mechanisms are operative in the case of ruthenium. Reaction of **1** with ruthenium trichloride hydrate affords after column chromatography on silica gel the novel bisaldehyde complex RuCl$_2$(PCHO)$_2$ (**6**),[16] which was isolated in 7% yield as deep purple needles.[17] Infrared spectroscopy indicates that the chlorides are trans for **6**, while the ^{1}H NMR shows the characteristic "filled-in doublet" virtual coupling pattern for the formyl protons which is most consistent with the coupling of a phosphorus trans to the formyl group in addition to the intraligand phosphorus coupling (J_{PH} for **1** is 5.5 Hz).[9] This geometry has been found crystallographically by us for the red complex *trans,cis*-RuCl$_2$(*o*-Ph$_2$PC$_6$H$_4$OCH$_3$)$_2$ which also possesses the Cl$_2$–P$_2$–O$_2$ donor set.[18] Compound **6** is a unique example of an exchange inert bisaldehyde complex,[19] showing no reaction at room temperature with carbon monoxide, 1,2-bis(diphenylphosphino)ethane, or pyridine (neat). Thermolysis of **6** at 220 °C results in rapid and quantitative formation of *cis,cis,trans*-RuCl$_2$(CO)$_2$(PPh$_3$)$_2$, the identity of which was confirmed by comparison with an authentic sample.[20] We assume that this reaction is intramolecular (no melting occurs) and it is clear that it proceeds via a pathway different from that found for Pt(II), as no HCl is evolved, or oxidative addition which would require the intermediacy of an eight-coordinate ruthenium(IV) complex. The geometry of the product is that of the thermodynamically most stable isomer of RuCl$_2$(CO)$_2$(PPh$_3$)$_2$ and does not necessarily reflect the stereochemical course of this decarbonylation. Under the conditions of the experiment *trans*-RuCl$_2$(CO)$_2$(PPh$_3$)$_2$ isomerizes to *cis,cis,trans*-RuCl$_2$(CO)$_2$(PPh$_3$)$_2$.[21]



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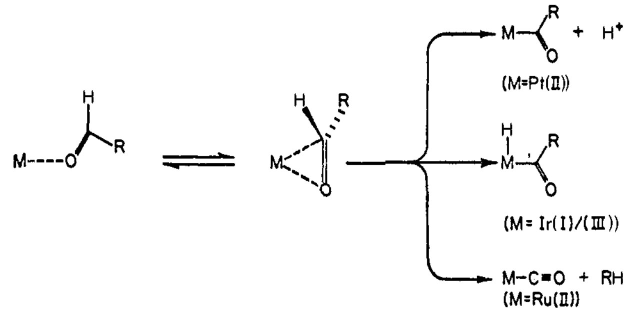
A mechanism which encompasses the platinum(II), iridium(I), and ruthenium(II) reactions is presented in Scheme I and involves the formation of the π-bonded carbonyl[22] which

Scheme I. Suggested Mechanism for the Reactions of Transition Metal–Aldehyde Complexes



can rearrange via hydrogen migrations to each of the observed products with minimal geometric reorganizations.[23]

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(11) Anal. Calcd for $C_{38}H_{29}ClO_2P_2Pt$: C, 56.32; H. 3.58; Cl, 4.38; P, 7.66. Found: C, 56.08; H, 3.59; Cl, 4.59; P, 7.90. Spectral data: IR (Nujol) 1695, 1625 cm^{-1}; ^1H NMR (90 MHz, $COCl_3$) τ −0.566 (d, 1 H, J_{PH} = 2 Hz), 2.0–3.0 (m, ~28 H); $^{31}P[^1H]$ (CH_2Cl_2) τ 30.12 (d), 48.54 (d) (J_{AB} = 391 Hz). For these and other ^{31}P data, downfield shifts are positive.

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(14) This mechanism was recently demonstrated by Suggs in the reaction of quinoline-8-carboxaldehyde with rhodium(I).[6]

(15) Spectral data: IR (Nujol) 2110 (w), 1635 cm^{-1} (s); ^1H NMR (90 MHz, $CDCl_3$) 2.0–2.9 (m, 14 H, Ph–H), 4.5 (m, 1 H, olefin), 5.0 (m, 2 H, olefin), 5.7 (m, 1 H, olefin), 7.5 (m, ~8 H, alkyl), 26.12 (d, 1 H, J_{PH} = 15 Hz).

(16) Anal. Calcd for $C_{38}H_{30}Cl_2O_2P_2Ru$: C, 60.32; H, 3.97; Cl, 9.11; P, 9.51. Found: C, 60.48; H, 3.88; Cl, 9.71; P. 9.14. Spectral data: IR (CH_2Cl_2) 1646 cm^{-1} (s); IR (Nujol) 372 cm^{-1} (m); ^1H NMR (90 MHz in $CDCl_3$) τ 0.6 (J_{PH} = 9 Hz, 2 H), 2.9–4.1 (m, 28 H); $^{31}P[^1H]$ τ 51.7(s).

(17) Purple ruthenium(II)–phosphine complexes have recently attracted attention, as they are usually five-coordinated and often catalytically active. See M. A. A. F. de C. T. Carrondo, B. N. Chaudret, D. J. Cole-Hamilton, A. C. Skapski, and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 463 (1978), and references therein.

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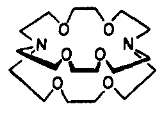
Synthesis and X-ray Structure of $N[(CH_2)_2O(2,6\text{-}C_6H_3N)O(CH_2)_2]_3N$: a D_3 Macrobicyclic Ligand Capped by Two sp^2 Nitrogen Atoms

Sir:

In 1970 (in a preliminary form), Weiss et al.[1] reported the molecular structure of the noncomplexed diazabicyclopolyether **1** (C-2.2.2) as well as of the corresponding rubidium cryptate **2** [$Rb^+ \subset 2.2.2$]. The free ligand **1** was shown to possess the endo-endo (in-in)[2] N configurations, in which the N–N distance was 6.872 (9) Å, a value slightly larger than that of **2** (6.008 Å).[1] In free cryptands, it has been generally assumed that the N lone pairs are either in the in-in, in-out, or out-out configurations.[3] In published structural representations of cryptands, these molecules are generally depicted in the in-in configuration for convenience in seeming correlation with the corresponding cryptates. However, a brief synopsis of cryptand literature suggests that few researchers are aware of the Weiss et al.[1] paper, since ~30–40% of the structural representations of C-2.2.2 are inadvertently and/or erroneously drawn in the out-out configuration. The correctness of the generally accepted concept of describing cryptand bridging nitrogen atoms as being only in the in or out configuration is now in question, since we herein report the X-ray crystal structure of **3**, in which *the bridgehead nitrogen atoms possess a planar configuration with crystallographically equivalent 120° bond angles.*



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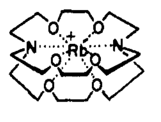

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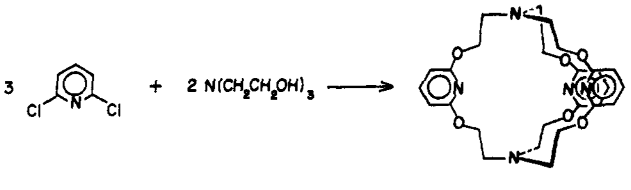

3

To a mixture of triethanolamine (10 mmol) with excess oil-free sodium hydride in xylene, 2,6-dichloropyridine **4** (15 mmol) in xylene was added. The mixture was refluxed for 36 h and worked up by previously described procedures[4] to afford (5%) **3**, as colorless crystals:[5] mp 228 °C dec; NMR (100 MHz) ($CDCl_3$) δ 3.08 (t, NCH_2, J = 6 Hz, 12 H), 4.32 (t, OCH_2, J = 6 Hz, 12 H), 6.13 (d, 3,5-PyrH, J = 8 Hz, 6 H), 7.30 (t, 4-PyrH, J = 8 Hz, 3 H); IR (KBr) 1580, 1250, 1145 cm^{-1}; UV (CH_3CN) λ_{max} 276 (3.10×10^6), 258 (sh, 2.36×10^6), 225 (7.50×10^6); mass spectrum m/e 523 (M^+), 412 ($M^+ - 111$). Numerous other macrocycles and oligomeric products were isolated and characterized.[6]

The molecular structure of **3** was established by X-ray crystallographic methods indicating: Trigonal space group $R\bar{3}c$, with rhombohedral axes a = 10.937 (2) Å, α = 83.33 (2)°, Z = 2, d_c = 1.355 g cm^{-3}, R = 0.060 for 430 unique observed data collected on an Enraf-Nonius CAD-4 diffractometer. The macrobicyclic cryptand **3** has been found to possess D_3 symmetry in the crystal, deviating from ideal D_{3h} symmetry by a slight twist about the C_3 axis (Figure 1). Figure 2 shows that all bond distances and angles are near their expected values except for the very surprising C–N–C angle of 120 ± 0.5° for the bridgehead, amine nitrogen atoms. Figure 3 shows a stereoscopic view of **3**.

Thus, since cryptand nitrogen atoms in **3** are planar sp^2

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