OXIDATIVE ADDITION OF ACID CHLORIDES TO CATIONIC RHODIUM(I) COMPLEXES OF CHELATING DIPHOSPHINES

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## Summary

The reaction of benzoyl chloride with $[Rh(dppp)_2]Cl$ at 190°C and with $[Rh(dppp)Cl]_{1 \text{ or } 2}$ at 25°C where dppp = 1,3-bis(diphenylphosphino)propane has been examined. In both cases the five coordinate compound $RhCl_2(COPh)$-(dppp) was rapidly formed and isolated in high yield. This compound does not undergo phenyl migration to $RhCl_2(CO)(Ph)(dppp)$ even upon warming to 190°C in benzoyl chloride solution and no decarbonylation products are observed. This is in marked contrast to the reaction of $RhCl(PPh_3)_3$ with benzoyl chloride where the migrated product $RhCl_2(CO)(Ph)(PPh_3)_2$ is formed with the eventual reductive elimination of chlorobenzene. The single crystal X-ray analysis of $RhCl_2(COPh)(dppp)$ has been carried out ($R = 0.036$). The compound is square pyramidal with the COPh group in the apical position. The Rh—C bond distance of 1.992(3) Å is short for a Rh^{III}—C_σ bond and indicates $d_\pi \rightarrow \pi^*$ back bonding.

Introduction

The catalytic homogeneous decarbonylation of aldehydes using complexes of the type $[Rh(dppp)_2]Cl$ (I) or $[Rh(dppp)Cl]_{1 \text{ or } 2}$ (II) where dppp = 1,3-bis(diphenylphosphino)propane has recently been reported [1,2]. Complex I is effective and useful for decarbonylating various aldehydes catalytically at temperatures as low as 115°C (Scheme 1). The only spectroscopically detectible intermediate in this reaction is $Rh(dppp)_2CO^+$ (III) [3] which may be isolated from the catalytic reaction mixture [1,2]. Importantly, complex I or III decarbonylates aldehydes selectively with catalytic activities which exceed those obtained using $RhCl(PPh_3)_3$ (IV) [4—6] by more than two orders of magnitude. Complex II [7] * is also an effective aldehyde decarbonylation

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* The nature of II in solution is best described as a monomer—dimer equilibrium: $[Rh(dppp)Cl] \rightleftharpoons [Rh(dppp)Cl]_2$.

SCHEME 1
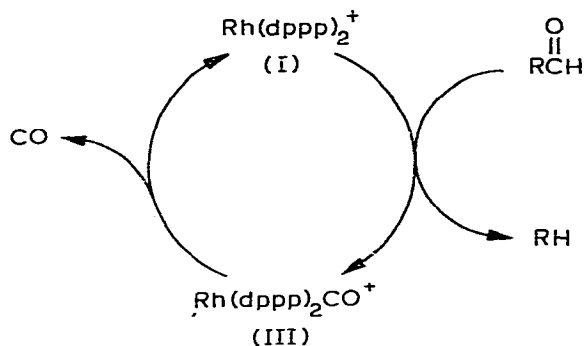
catalyst but with lower activity and stability than I [2]. Complex IV is effective at decarbonylating acid chlorides, and in this case the reaction mechanism is thought to be well understood (Scheme 2) [8,9]. Intermediates V and VI have been isolated and characterized [8,9]. Complex V with $R = CH_2C_6H_5$ and

SCHEME 2
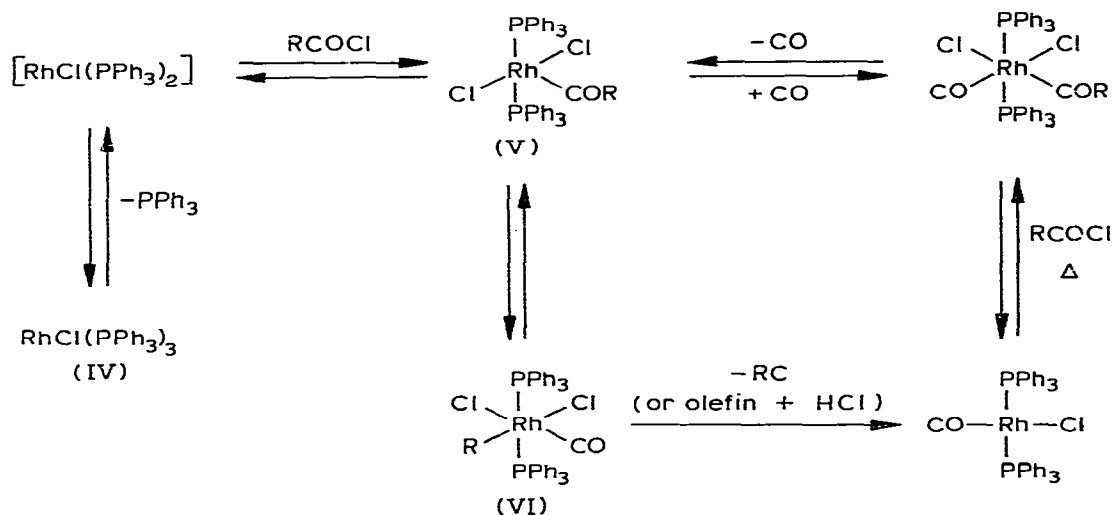
$CH_2CH_2C_6H_5$ has been structured by two independent single crystal X-ray analyses with conflicting results [8,9]. The former compound ($R = CH_2C_6H_5$) was claimed to be trigonal bipyramidal [8] while the latter ($R = CH_2CH_2C_6H_5$) appears to be square pyramidal [9]. However, neither structure is of the quality necessary for a highly accurate determination of the coordination geometry and therefore some uncertainty remains as to the structural nature of this important class of compounds *,

As part of our studies designed to elucidate the mechanism of the reaction

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* X-ray structural results on these two compounds were only reported at a preliminary stage of refinement (R values of 0.20 and 0.18 for the $COCH_2C_6H_5$ [8] and $COCH_2CH_2C_6H_5$ [9] analogues, respectively) and no further details have been published to date.

shown in Scheme 1, the decarbonylation of acid chlorides was attempted. Surprisingly, reaction of acid chlorides with I or with II under a purified N_2 atmosphere did not lead to decarbonylation products even at temperatures as high as 190°C, in marked contrast to the rapid decarbonylation observed with IV (Scheme 2). However, a rapid oxidative addition reaction did occur between neat benzoyl chloride and I at 190°C under a N_2 atmosphere yielding a yellow solution from which a solid product was precipitated in >95% yield by the rapid addition of decane. The compound is formulated as $RhCl_2(COPh)(dppp)$ by elemental analysis (found: C, 59.31; H, 4.71. $Rh_1Cl_2P_2C_{34}H_{31}O$ calcd.: C, 59.20; H, 4.50%) and by IR spectroscopy, KBr disk (ν(CO) 1641 cm^{-1}). The same compound can be synthesized in high yield by reaction of benzoyl chloride with II in CH_2Cl_2 solution at 25°C. This method of synthesis is essentially the same as reported by Baird for $RhCl_2(COMe)(dppp)$ [10].

Experimental

Crystals suitable for single crystal X-ray analysis were obtained by slow evaporation from CH_2Cl_2/heptane solution. Crystals of $RhCl_2(COPh)(dppp)$ belonged to the triclinic crystal class with a 9.264(5), b 10.882(3), c 15.907(5) Å, α 97.41(4), β 104.95(3) and γ 94.66(4)° as determined from a least-squares refinement of the angular settings of 25 reflections centered accurately on an Enraf-Nonius CAD4 diffractometer. Successful solution and refinement was achieved using the centric space group $P\bar{1}$ (V 1524 Å^3, Z = 2). A total of 5355 unique reflections were measured in the scan range 2θ = 0—50° on an Enraf-Nonius CAD4 automatic diffractometer using graphite monochromatized Mo-K_α radiation (Mo-K_α, λ 0.71069 Å) and employing a variable rate ω—2θ scan technique. No decay was noted in the intensities of three standard reflections recorded at intervals of 200 sequential reflections. After correction for Lorentz, polarization, absorption (μ 8.5 cm^{-1}), and background effects, 4385 (82%) were judged observed ($F_0^2 \geqslant 3\sigma(F_0^2)$) and were used in all subsequent calculations *.

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* The intensity data were processed as described in the "CAD4 and SDP Users Manual", Enraf-Nonius, Delft, Holland, 1978. The net intensity I is given as

$$I = \frac{K}{NPI}(C - TB)$$

where K = 20.1166 (attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, B = total background count and T = the ratio of total count time to background count time and is 2. The standard deviation in the net intensity is given by

$$\sigma^2(I) = \left(\frac{K}{NPI}\right)^2 [C + 4B + (pI)^2]$$

where p is a factor used to downweight intense reflections. The observed structure factor amplitude F_0 is given by

$$F_0 = (I/Lp)^{1/2}$$

where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_0)$ by

$$\sigma(F_0) = 1/2 \frac{\sigma(I)}{I} F_0.$$

All calculations were carried out on a PDP 11/34 computer using the Enraf-Nonius SDP programs. This crystallographic computing package is described in the following reference. B.A. Frenz, "The Enraf-Nonius CAD4 SDP-A Real Time System for Concurrent X-Ray Data Collection and Crystal Structure Determination", in Computing in Crystallography, H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld, and G.C. Bassi, Eds., Delft University Press, Delft, Holland, 1978, pp. 64—71.

TABLE 1

POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS.

ATOM	X	Y	Z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
RH	0.16298(3)	0.24609(3)	0.25364(2)	0.00727(3)	0.00445(2)	0.0025(1)	0.0019(5)	0.00160(3)	0.00002(3)
CL1	-0.0005(1)	0.3305(1)	0.1412(6)(7)	0.0137(2)	0.0047(9)	0.0032(4)	0.0005(2)	-0.0007(1)	0.0021(1)
CL2	-0.0433(1)	0.1956(1)	0.3121(6)(7)	0.0085(1)	0.0072(9)	0.0043(4)	0.0018(2)	0.0044(1)	0.0028(1)
P1	0.3414(1)	0.26475(10)	0.1782(6)(7)	0.0101(1)	0.0059(8)	0.0027(4)	0.0008(2)	0.0035(1)	0.00078(10)
P2	0.2835(1)	0.11267(9)	0.33830(7)	0.0075(1)	0.0059(8)	0.0031(4)	0.0034(2)	0.0026(1)	0.00241(9)
O1	0.4100(3)	0.4134(3)	0.3631(2)	0.0091(4)	0.0086(3)	0.0044(1)	-0.0022(6)	0.0032(4)	-0.0016(3)
C1	0.2742(5)	0.3932(4)	0.3412(2)	0.0113(5)	0.0051(3)	0.0026(1)	0.0006(7)	0.0021(5)	0.0010(4)
C2	0.1821(5)	0.4703(3)	0.3821(3)	0.0189(5)	0.0046(3)	0.0034(2)	0.0019(7)	0.0029(5)	0.0006(4)
C3	0.2549(5)	0.5474(4)	0.4650(3)	0.0119(6)	0.0075(4)	0.0041(2)	-0.0012(8)	0.0035(6)	-0.0013(5)
C4	0.1799(6)	0.6323(5)	0.5054(3)	0.0137(6)	0.0086(4)	0.0046(2)	0.0003(9)	0.0046(6)	-0.0027(5)
C5	0.0340(6)	0.6519(4)	0.4636(3)	0.0153(7)	0.0074(4)	0.0053(2)	0.0041(9)	0.0056(6)	-0.0012(5)
C6	-0.0376(6)	0.5880(5)	0.3813(3)	0.0157(7)	0.0079(4)	0.0056(3)	0.0009(9)	0.0027(7)	-0.0006(6)
C7	0.0351(5)	0.4962(4)	0.3410(3)	0.0126(6)	0.0070(4)	0.0041(2)	0.0053(8)	0.0014(6)	-0.0007(5)
C8	0.5317(5)	0.2374(4)	0.2348(3)	0.0073(5)	0.0093(4)	0.0044(2)	0.0016(8)	0.0028(5)	0.0026(5)
C9	0.5383(5)	0.1118(5)	0.2697(3)	0.0097(5)	0.0106(4)	0.0044(2)	0.0054(8)	0.0056(5)	0.0029(5)
C10	0.4067(5)	0.1202(4)	0.3554(3)	0.0073(5)	0.0105(4)	0.0040(2)	0.0045(8)	0.0032(5)	0.0036(5)
C11	0.3602(6)	0.4144(4)	0.1397(3)	0.0102(7)	0.0078(4)	0.0041(2)	0.0013(9)	0.0093(5)	0.0020(5)
C12	0.4909(8)	0.5814(5)	0.1034(4)	0.0322(11)	0.0084(5)	0.0062(2)	-0.0091(12)	0.0139(8)	0.0007(6)
C13	0.5078(10)	0.6174(6)	0.1522(5)	0.0448(16)	0.0098(6)	0.0089(4)	-0.0081(16)	0.0166(11)	0.0025(8)

C14	0.3920(9)	0.6401(6)	0.0778(4)	0.0406(14)	0.0131(6)	0.0093(3)	0.0000(16)	0.0235(9)	0.0099(7)
C15	0.2806(9)	0.5540(6)	0.0360(4)	0.0369(12)	0.0151(6)	0.0089(3)	0.0194(15)	0.0221(9)	0.0136(6)
C16	0.2633(7)	0.4391(5)	0.0650(3)	0.0257(9)	0.0137(5)	0.0055(2)	0.0146(12)	0.0114(7)	0.0094(6)
C17	0.2991(5)	0.1508(4)	0.0784(3)	0.0108(5)	0.0073(4)	0.0032(2)	0.0030(8)	0.0031(5)	-0.0004(4)
C18	0.3718(7)	0.1640(6)	0.0133(3)	0.0230(9)	0.0138(6)	0.0056(2)	-0.0060(12)	0.0140(6)	-0.0046(6)
C19	0.3458(6)	0.0720(7)	-0.0590(4)	0.0248(10)	0.0176(8)	0.0065(3)	-0.0037(16)	0.0139(8)	-0.0065(8)
C20	0.2506(6)	-0.0357(5)	-0.0676(4)	0.0148(7)	0.0124(5)	0.0053(2)	0.0071(11)	0.0030(7)	-0.0043(6)
C21	0.1800(7)	-0.0528(5)	-0.0023(4)	0.0174(8)	0.0107(5)	0.0049(2)	-0.0024(11)	0.0041(7)	-0.0046(6)
C22	0.2027(6)	0.0425(5)	0.0695(3)	0.0169(8)	0.0096(5)	0.0049(2)	-0.0033(11)	0.0059(7)	-0.0026(6)
C23	0.2002(5)	-0.0402(4)	0.2077(3)	0.0114(5)	0.0052(3)	0.0041(2)	0.0033(7)	0.0050(5)	0.0033(4)
C24	0.0655(6)	-0.0768(4)	0.2294(3)	0.0158(7)	0.0062(4)	0.0054(2)	-0.0000(9)	0.0027(7)	0.0007(5)
C25	0.0103(8)	-0.1989(5)	0.1888(4)	0.0245(10)	0.0082(5)	0.0062(3)	-0.0046(12)	0.0076(8)	-0.0008(6)
C26	0.0999(8)	-0.2927(5)	0.2054(4)	0.0282(10)	0.0057(4)	0.0094(3)	0.0012(11)	0.0162(9)	0.0006(6)
C27	0.2305(8)	-0.2669(5)	0.2645(5)	0.0246(10)	0.0067(4)	0.0127(4)	0.0095(11)	0.0157(10)	0.0061(7)
C28	0.2962(7)	-0.1453(5)	0.3054(4)	0.0197(8)	0.0072(4)	0.0089(3)	0.0095(10)	0.0101(8)	0.0057(6)
C29	0.2718(4)	0.1244(4)	0.4516(3)	0.0077(5)	0.0004(4)	0.0034(2)	0.0064(7)	0.0023(5)	0.0034(4)
C30	0.1948(5)	0.0293(4)	0.4788(3)	0.0100(5)	0.0107(4)	0.0042(2)	0.0054(8)	0.0038(5)	0.0061(4)
C31	0.1904(6)	0.0411(5)	0.5670(3)	0.0122(6)	0.0136(5)	0.0046(2)	0.0086(10)	0.0046(6)	0.0074(5)
C32	0.2638(6)	0.1442(5)	0.6270(3)	0.0148(6)	0.0160(6)	0.0039(2)	0.0148(10)	0.0062(6)	0.0070(5)
C33	0.3422(6)	0.2400(5)	0.6005(3)	0.0154(7)	0.0130(5)	0.0036(2)	0.0137(10)	0.0031(6)	0.0022(5)
C34	0.3400(5)	0.2308(4)	0.5119(3)	0.0132(6)	0.0097(4)	0.0034(2)	0.0000(9)	0.0022(6)	0.0029(5)

THE FORM OF THE ANISOTROPIC THERMAL PARAMETER IS:

EXP[-(B(1,1)*H*H + B(2,2)*K*K + B(3,3)*L*L + B(1,2)*H*K + B(1,3)*H*L + B(2,3)*K*L)].

A three-dimensional Patterson function revealed the position of the rhodium
atom. Fourier and difference Fourier analysis revealed the positions of all
remaining nonhydrogen atoms. Full matrix least-squares refinement with all
40 nonhydrogen atoms refined anisotropically (361 variables, 4385 observations)
converged to final R and R_w values of 0.036 and 0.054, respectively *. The
error in an observation of unit weight was 1.71 using a value of 0.05 for p in the
$\sigma(I)$ equation *. In the final difference Fourier, the highest peak was 0.63
electrons $Å^{-3}$ and corresponded to a H atom position. The final values of the
positional and thermal parameters are given in Table 1 **. Scattering factor
tables and anomalous dispersion terms (included for all refined atoms) were
obtained from the "International Tables for X-Ray Crystallography", Birming-
ham, 1974, Tables 2.2B and 2.3.1, respectively. Hydrogen atoms were not
located nor included in the structure factors.

Discussion

The crystal structure consists of discrete molecules of $RhCl_2(COPh)(dppp)$.
The coordination geometry about rhodium is square pyramidal with the benzoyl
group occupying the apical position. A view of the coordination geometry is
presented in Fig. 1 along with the important intramolecular distances and
angles. The numbering scheme used on the dppp phenyl groups (not shown in
Fig. 1) is C(11)—C(16) and C(17)—C(22) connected via C(11) and C(17) to
P(1), and C(23)—C(28) and C(29)—C(34) connected via C(23) and C(29) to
P(2). An ORTEP stereoview of the entire molecule is shown in Fig. 2. The
square pyramidal geometry is confirmed by an examination of the cis-ligand—Rh—
ligand angles which average 93°, with maximum and minimum values of 105
and 86°. The P(2), P(2), Cl(1), Cl(2) atoms are within ±0.06 Å of their weighted
least-squares plane while the Rh atom is displaced 0.26 Å from this plane
towards the benzoyl group. The coordination geometry is similar to that of
[RhI(COEt)(PPh₃)(mnt)]⁻ where mnt = maleonitriledithiolate [11]. The Rh—C
distance of 1.992(3) Å is slightly shorter than other Rh—C_σ bonds [11—13]
except those of the Rh—$C_{carbene}$ type [14,15]. Rh—$C_{carbene}$ distances range
from 1.930(6) [14] to 1.968(13) Å [15] while previously reported rhodium(III)—
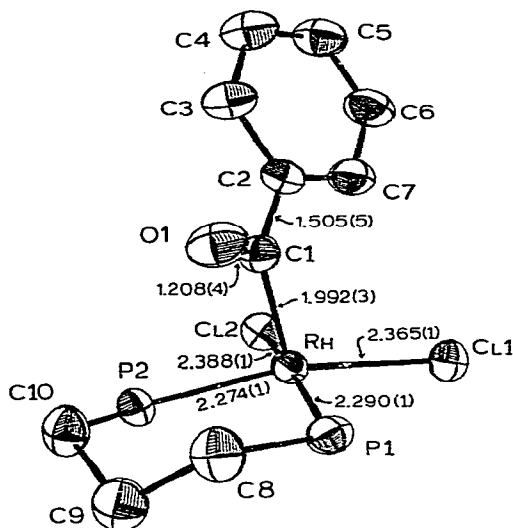COR distances range from 2.001(7) [16] to 2.06(2) Å [17]. The shortness of

Fig. 1. ORTEP drawing of the coordination core of RhCl₂(COPh)dppp with selected bond distances in Å and their estimated standard deviations in parentheses. Angles in the coordination core are: P(1)—Rh—P(2), 94.23(3)°; P(1)—Rh—Cl(1), 87.72(3); P(2)—Rh—Cl(2), 85.61(3); Cl(1)—Rh—Cl(2), 89.60(3); Cl(1)—Rh—P(2), 163.52(3); Cl(2)—Rh—P(1), 169.78(3); C(1)—Rh—P(1), 89.15(10); C(1)—Rh—P(2), 91.26(9); C(1)—Rh—Cl(1), 105.14(9); C(1)—Rh—Cl(2), 101.07(10).

the Rh—C bond indicates that metal to ligand ($d_\pi \rightarrow \pi^*$) back bonding is probably important [13,16]. The distances and angles within the dppp and benzoyl ligands are normal.

The difference in chemical reactivity between RhCl₂(COPh)(PPh₃)₂ (V) and RhCl₂(COPh)(dppp) is quite remarkable. The former compound, which apparently has a square pyramidal geometry with COPh apical and *trans*-PPh₃ groups, undergoes phenyl migration to RhCl₂(CO)(Ph)(PPh₃)₂ (VI) at room
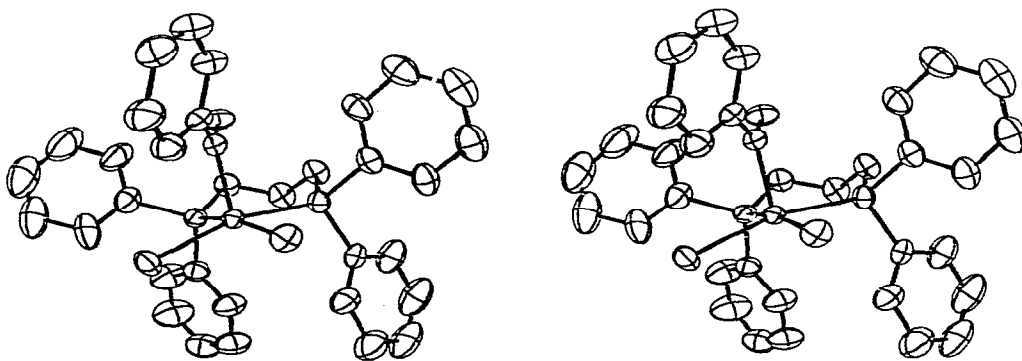

Fig. 2. ORTEP stereoview of RhCl₂(COPh)dppp.

temperature in 1,2-dichloroethane with eventual production of chlorobenzene [18] whereas $RhCl_2(CO)(Ph)(dppp)$ is not observed nor is chlorobenzene produced from $RhCl_2(COPh)(dppp)$ even after heating to 190°C in benzoyl chloride solution. Baird at al. [10] have also noted the inability of $RhCl_2(COMe)$-(dppp) to undergo Me group migration in refluxing $CDCl_3$ solution. An explanation for this reactivity difference could be the shortness of the Rh—C bond in $RhCl_2(COPh)dppp$ which indicates that Rh—COPh bonding is quite stable. Additionally, the short Rh—C distance would cause a *trans* effect [14] which may prevent isomerization of a chloride or phosphine ligand to this *trans* site. Such an isomerization is presumably necessary prior to phenyl migration to an open *cis* coordination site. An accurate structural determination of V is necessary in order to test this possibility. Alternatively, the presence of the chelating diphosphine ligand may limit certain isomerisation pathways which are necessary for migration, or perhaps the resulting octahedral complex, $RhCl_2(CO)$-(Ph)(dppp), in which the phenyl group is *trans* to a phosphorus, is not stable relative to $RhCl_2(COPh)(dppp)$ [10]. Additional experiments are needed in order to decide between these alternatives.

It is important that benzaldehyde is catalytically decarbonylated to benzene by II at 115°C [2], whereas no chlorobenzene is produced from benzoyl chloride in the presence of this catalyst even at 190°C (vide supra). The difference in reactivity between benzaldehyde and benzoyl chloride is not due to the inability of the latter to undergo oxidative addition (vide supra) but must be due to a greatly increased migrating ability of the phenyl group in $Rh(H)(Cl)$-(COPh)(dppp) compared with $RhCl_2(COPh)(dppp)$. Perhaps the presence of the hydride (a strong *trans* effect ligand) induces fission of the *trans*-Rh—P bond which would provide an open *cis* site for migration. The unusual stability of $RhCl_2(COPh)(dppp)$ is further demonstrated by the observation that the addition of a small amount of benzoyl chloride to a benzaldehyde solution of II at 145°C immediately stops the catalytic production of benzene.

It is also noteworthy that in the formation of $RhCl_2(COPh)(dppp)$ from $[Rh(dppp)_2]Cl$ and PhCOCl, a dppp ligand has been lost. During catalytic decarbonylation of aldehydes using $[Rh(dppp)_2]Cl$ there is no evidence for dppp loss. Indeed, the catalyst may be quantitatively recovered even after 100000 turnovers at 150°C and there are no spectroscopically observable intermediates save for $Rh(dppp)_2CO^+$ (vide supra) [1,2]. Although it is probable and resonable that Rh—P bond rupture occurs in Scheme 1 giving intermediates with monodentate dppp [2], it is unlikely that complete dppp dissociation is important. Additionally, the catalytic activity (turnovers/hour) for aldehyde decarbonylation using (II) is a factor of 10 smaller than with I [2]. Experiments in progress are directed at determining the mechanisms of these reactions.

Acknowledgement

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