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Arene C–H bond activation: reaction of $(Me_3P)_3Rh(Me)$ with toluene to give $(Me_3P)_3Rh(Ar)$ where Ar is *o*-, *m*- and *p*-tolyl

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Abstract

The square-planar rhodium (I) compound, $(Me_3P)_3Rh(Me)$, reacts with benzene or toluene at 70° to give $(Me_3P)_3Rh(Ph)$ or $(Me_3P)_3Rh(Ar)$ where Ar is *o*-, *m*-, *p*-tolyl along with methane. These aryl compounds were prepared independently and characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The benzyl compound, prepared from $PhCH_2Li$ and $(Me_3P)_3RhCl$, is formulated as an η^3-benzyl, is not formed in detectable amounts in the arene activation studies. The benzyl compound rearranges on heating to $(Me_3P)_3Rh(o\text{-tolyl})$ in near quantitative yield at 70 °C. The four-coordinate compound, $(Me_3P)_3Rh(Me)$, is fluxional at +20° though the fluxional process is stopped at −20 °C. The five-coordinate compound, $(Me_3P)_4Rh(Me)$, also is fluxional at +20 °C though stereochemical rigid at −65 °C. The geometry of the latter compound is based upon a trigonal bipyramid with the methyl group on the axial site.

Intermolecular insertion of C–H bonds of aromatic or aliphatic hydrocarbons into metal atoms of coordination compounds to yield compounds with metal–carbon and metal–hydrogen bonds, or reaction products formed therefrom, is a topic of considerable current interest since the first observation of aromatic C–H activation [1]. We have shown recently that the simple, square-planar, rhodium (I) compound, $(cod)Rh(Me)(PR_3)$, react with benzene or toluene, though not with tetramethylsilane nor methane, at 70 °C to give $(cod)Rh(Ph)(PR_3)$ or $(cod)(Rh(m\text{-tolyl})(PR_3)$ and $(cod)Rh(p\text{-tolyl})(PR_3)$, respectively. The rates of reaction are so slow, $t_{1/2}$ of ca. 100 h, that other thermal processes occur at comparable rates and the activation reaction is a laboratory curiosity rather than a useful chemical reaction [2]. In order to gain some qualitative understanding of this reaction we studied the reaction of

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complexes in which the sterically small, π-acceptor 1,5-cyclooctadiene ligand was replaced by the σ-donor alkylphosphine ligand, $R_2PCH_2CH_2PR_2$. The compound, $(Me_3C)_2PCH_2CH_2P(CMe_3)_2Rh(Me)(PMe_3)$, does not react with benzene to any observable extent (^1H NMR spectroscopy) at 100 °C for 1 week, though the less sterically crowded compound, $(Me_2HC)_2PCH_2CH_2P(CHMe_2)_2Rh(Me)(PMe_3)$, does react under these conditions, but the rate is slower than that observed in the 1,5-cyclooctadiene compound [3]. Since these observations indicate that steric effects are important, we tried, unsuccessfully, to make $(Me_2PCH_2CH_2PMe_2)Rh(Me)(PMe_3)$, though the monodentate, tris-phosphine analogue, $(Me_3P)_3Rh(Me)$, is well-known [4]. We were intrigued by the reactions, eq. 1 and 2, the outcome of which depends upon the solvent [4].

$$(Me_3P)_4RhCl + MeLi \xrightarrow{Et_2O,\ 0\,^\circ C} (Me_3P)_3RhMe + LiCl \quad (1)$$

$$(Me_3P)_4RhCl + MeLi \xrightarrow{PhMe,\ reflux} (Me_3P)_3Rh(m\text{-tolyl}) \quad (2)$$

The authors [4] suggested that the tolyl compound is formed by the following set of reactions (eq. 3 and 4). This explanation is based upon the relative pKa's of methane and PhMe of ca. 56 and 43, respectively [5]. This explanation is unreasonable on the grounds that alkyllithium reagents metallate toluene slowly in diethyl ether though rapidly in presence of nitrogen-containing Lewis bases [6]. Further, in presence of $Me_2NCH_2CH_2NMe_2$, alkyllithium compounds metallate the aliphatic, not the aromatic, C–H bonds to give benzyllithium rather than the aryllithium compound [7].

Two additional pathways may be postulated to account for the results shown in eq. 2. These are shown in eq. 5, 6, 7 and in eq. 8.

$$MeLi + PhMe \rightarrow PhCH_2Li + MeH \quad (5)$$

$$(Me_3P)_4RhCl + PhCH_2Li \rightarrow (Me_3P)_3RhCH_2Ph + Me_3P + LiCl \quad (6)$$

$$(Me_3P)_3Rh(CH_2Ph) \rightarrow (Me_3P)_3Rh(tolyl) \quad (7)$$

$$(Me_3P)_3RhMe + PhMe \rightarrow (Me_3P)_3Rh(tolyl) + MeH \quad (8)$$

The rearrangement in eq. 7 is not unreasonable since aryl–metal bonds are ca. 10 kcal mol^{-1} stronger than alkyl–metal bonds for main group elements [8] and this trend appears to be true for the later d-transition metals, though the number of examples is rather small [9]. Further, the thermal rearrangement of a $PtCH_2CMe_2Ph$ to a Pt-o-$C_6H_4CMe_3$ group has been described recently [10]. The second alternative shown in eq. 8, is an arene activation reaction.

In this paper we show that $(Me_3P)_3RhMe$ reacts with benzene or toluene to give products of C–H activation.

Results and discussion

The aryl compounds that could be formed by C–H activation of benzene or toluene, $(Me_3P)_3Rh(R)$ where R is Ph, o-tolyl, m-tolyl, p-tolyl, or benzyl, have been

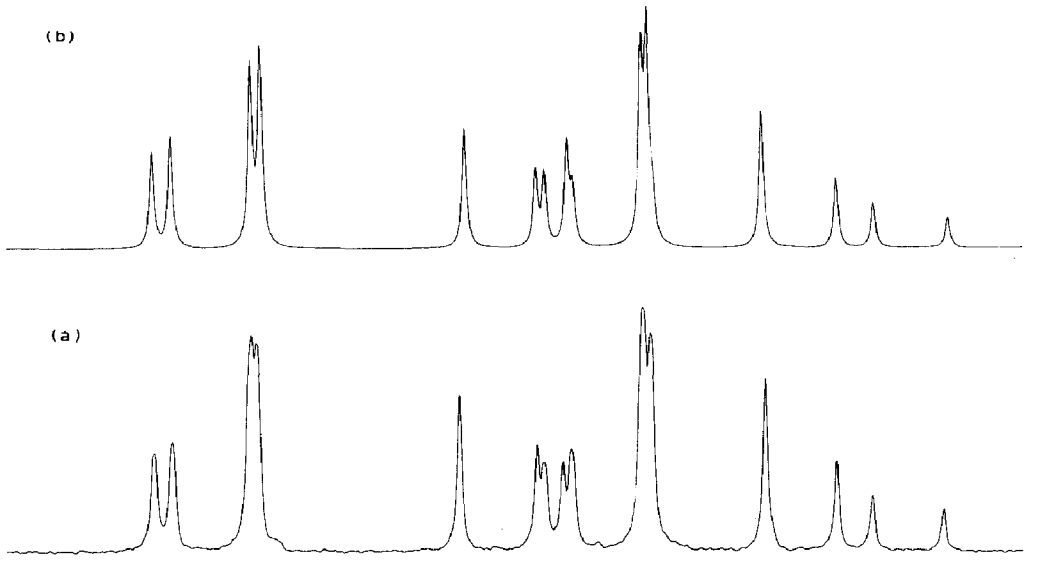

Fig. 1. (a) The observed 202 MHz $^{31}P\{^1H\}$ NMR spectrum of $(Me_3P)_3RhPh$; (b) the calculated 202 MHz $^{31}P\{^1H\}$ NMR spectrum of $(Me_3P)_3RhPh$.

prepared by metathetical exchange reactions as described in the Experimental section. The aryls are all square planar rhodium(I) compounds and their $^{31}P\{^1H\}$ NMR spectra at room temperature define the A_2BX spin system where A and B are phosphorus nuclei and X is the rhodium nucleus; chemical shifts and coupling constants are given in Table 1. The *o*-tolyl compound gives a rather complex appearing pattern in the $^{31}P\{H\}$ NMR spectrum at 82 MHz, but at 202 MHz the pattern is easily recognized as A_2BX, where $\delta(A) - \delta(B) = 1.41$ ppm, and the spectrum may be analyzed by inspection. The spectrum of the related neopentyl compound may be analyzed similarly. The $^3P\{^1H\}$ NMR spectra of the phenyl, *m*-tolyl, and *p*-tolyl compounds are indistinguishable and they appear to be rather complex at both 82 and 202 MHz. The 202 MHz spectrum of the phenyl compound is shown in Fig. 1a. The spectrum cannot be analyzed by inspection though the experimental spectrum can be simulated, Fig. Ib, with the values shown in Table 1. In the spectra of these compounds, the chemical shift difference, $\delta(A)$–$\delta(B) = 0.52$ ppm, is small though the coupling constants are similar, to those of the *o*-tolyl derivative. The small difference in chemical shift accounts for the difficulty in recognizing the A_2BX spin system even at high magnetic field. These three compounds all give distinct ^1H and $^{13}C\{^1H\}$ NMR spectra, each of which is consistent with their formulation (see Experimental Section for details) so the $^{31}P\{^1H\}$ NMR spectra are not averaged spectra due to some chemical exchange process or a mixture of the compounds, but their ^{31}P chemical shifts and coupling constants are indistinguishable within the natural line width at 202 MHz.

The spectra of the benzyl derivative require additional comment since they are temperature dependent. At $-50\,^\circ C$, the $^{31}P\{^1H\}$ NMR spectrum shows a A_2BX pattern, Table 1, though at $28\,^\circ C$ a broad resonance is observed that is a sharp single resonance at $+60\,^\circ C$. The large difference in chemical shift, $\delta(A) - \delta(B) = -8.06$ ppm, is unusual for the compounds listed in Table 1 and suggests that $(Me_3P)_3Rh(CH_2Ph)$ has an unusual structure, though one in which the phosphorus

Table 1

$^{31}P\{^1H\}$ NMR Spectra of $(Me_3P)_3RhR$ [a]

Compound R =	Temperature (°C)	Solvent	$\delta(P_A)$	$\delta(P_B)$	$^1J(P_ARh)$	$^1J(P_BRh)$	$^2J(P_AP_B)$
Me	−20	C_7D_8	−10.40	−15.74	151.0	122.7	36.2
CD_3	−40	C_6H_{12}	−10.40	−15.71	154.0	122.7	36.1
CH_2CMe_3	+22	C_7D_8	−17.08	−14.69	175.1	115.4	36.4
η^3-CH_2Ph	−50	C_7D_8	−16.03	−7.97	201.3	134.9	39.7
o-tolyl	+25	C_6D_6	−14.67	−16.08	151.4	114.6	35.3
Ph, *m*-tolyl, or *p*-tolyl	+20	C_7D_8	−14.99 [c]	−15.51	151.0	113.8	34.7

[a] Recorded at 82 MHz or 202 MHz, the chemical shifts are relative to 85% H_3PO_4, $\delta = 0$, and positive values are to high frequency. Coupling constants are expressed in hertz. [b] P_A represents the mutually *trans* PMe_3's, P_B represents the Me_3P that is *trans* to R. [c] See Fig. 1.

nuclei may be described as a A_2B portion of a A_2BX spin system. The ^1H NMR spectrum at 60 °C shows that the Me_3P resonances are equivalent and that they lose their coupling to Rh as do the benzylic methylene protons. These observations are consistent with a fluxional process that results in intermolecular trimethylphosphine site exchange. The $^{13}C\{^1H\}$ NMR spectrum at −50 °C is particularly informative relative to structure. At −50 °C, all of the carbons of the benzyl group show doublet coupling to a phosphorus nucleus, presumably the *trans* one, and coupling to rhodium and the other two phosphorus nuclei is not resolved except for the benzylic methylene carbon at δ 26.40 which is a doublet, ^2J(CP) 45.7 Hz, of doublets, ^1J(CRh) 13.2 Hz, of triplets, ^2J(CP) 6.5 Hz. The other carbon atoms are at δ 120.36, J(CP) 47.8 Hz, δ 122.64, J(CP) 45.0 Hz, 119.63, J(CP) 39.8 Hz, and δ 118.13, J(CP) 5.6 Hz due to the C(*ipso*), C(*ortho*), C(*meta*), and C(*para*), respectively, assigned on the basis of relative intensity and coupling to the hydrogen atom. The observed coupling in the $^{13}C\{^1\}$ NMR spectrum is consistent with an η^3-benzyl formulation in which there is a dynamic process that is still rapid at −50 °C that makes both sides of the η^3-benzyl group equivalent on the NMR time scale which effectively imposes C_s symmetry on the molecule. This compound, $(Me_3P)_3Rh(\eta^3$-benzyl), has been mentioned though no data were provided [12b]. A similar pattern in the NMR spectrum has been observed for $[(MeO)_3P]_3Co(\eta^3$-$CH_2Ph)$ [11a] and the X-ray structure shows that the benzyl group is bound to cobalt in an η^3-fashion [11b]. Isolation of the neopentyl and benzyl compounds of rhodium(I) is noteworthy since the corresponding iridium compounds cannot be isolated, metallocyclic compounds based upon iridium(III) being isolated instead [12].

The methyl compound, $(Me_3P)_3Rh(Me)$, is fluxional also, and the spectra reported in the paper which described its synthesis are averaged spectra [4]. The spectra at −20 °C are listed in Table 1 and in the Experimental section. There is some confusion in the literature about the existence of the five-coordinate complexes, $(Me_3P)_4Rh(Me)$ [13], and we describe our studies in detail. We have found that $(Me_3P)_4Rh(Me)$ is best made by addition of an excess of Me_3P to $(cod)_2Rh_2(\mu$-$Cl)_2$ followed by addition of MeLi at −65 °C, the details of which are given in the Experimental section. The tetraphosphine complex is yellow and the trisphosphine complex is orange. Both are fluxional on the NMR time scale at room

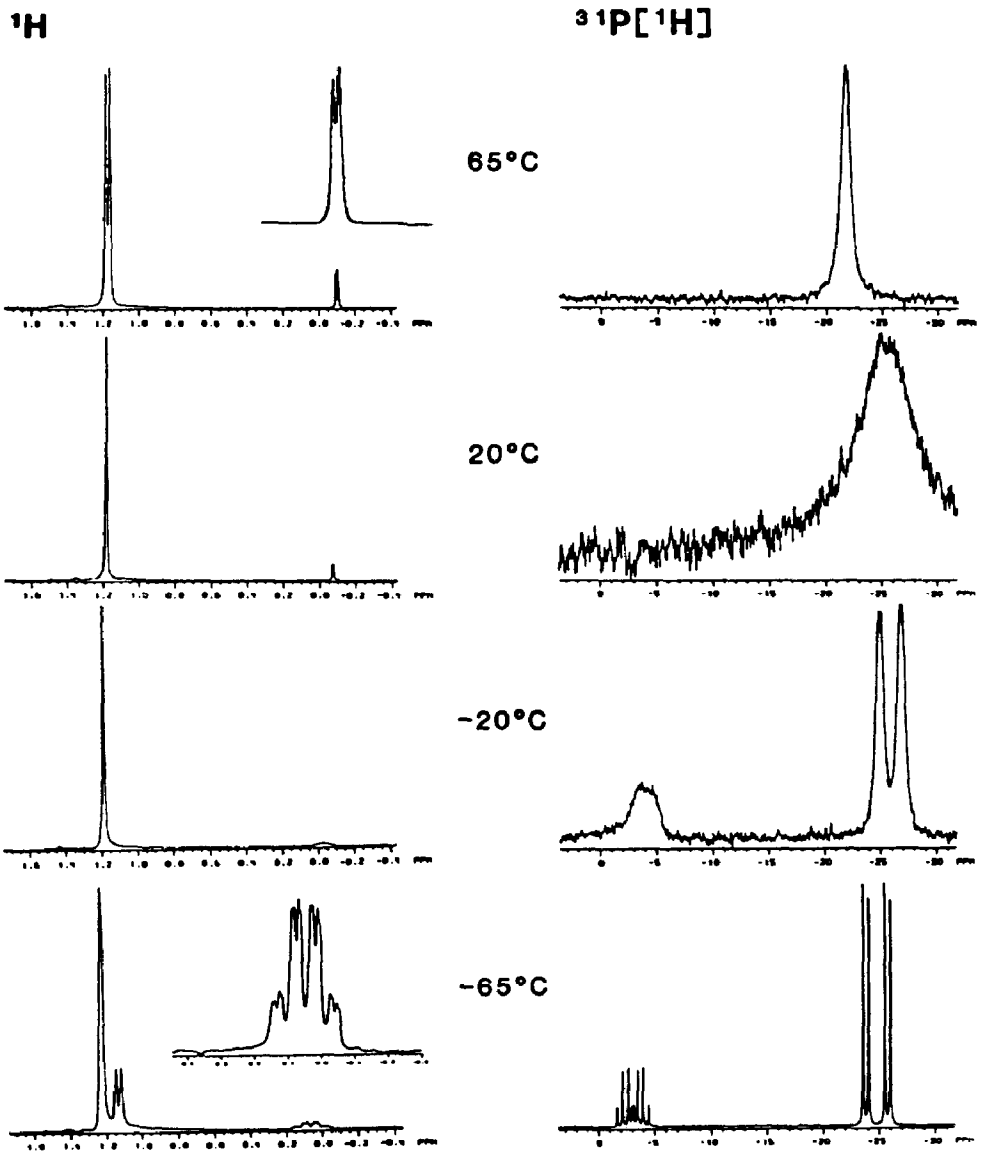

Fig. 2. The ^{1}H (202 MHz) and ^{31}P{^{1}H} (82 MHz) NMR spectra of $(Me_3P)_4RhMe$ at various temperatures in C_7D_8.

temperature though site exchange can be stopped at $-20\,^\circ C$ for $(Me_3P)_3Rh(Me)$ and at $-65\,^\circ C$ for $(Me_3P)_4Rh(Me)$. The ^{1}H and ^{31}P{^{1}H} NMR spectra for the latter compound are shown in Fig. 2. The ^{31}P{^{1}H} NMR spectrum of $(Me_3P)_4Rh(Me)$ at $-65\,^\circ C$ shows an A_3BX pattern, consistent with a trigonal bipyramidal geometry with the methyl group in the axial site. The equivalent phosphorus nuclei on the equatorial sites appear at δ −23.43 as a doublet, $^1J(P_ARh)$ 157.7 Hz, of doublets, $^2J(P_AP_B)$ 40.6 Hz. The axial phosphorus nucleus appears at δ −1.69 as a doublet, $^1J(P_BRh)$ 105.9 Hz, of quartets, $^2J(P_AP_B)$ 40.6 Hz. The Me–Rh resonance in the ^{1}H NMR spectrum at $-65\,^\circ C$ appears at δ 0.05 as a quartet, $^3J(HP_A)$ 11.5 Hz, of doublets, $^3J(HP_B)$ 4.2 Hz, of doublets, $^2J(HRh)$ 1.3 Hz and at δ

-8.33 in the $^{13}C\{^1H\}$ NMR spectrum as a doublet, $^2J(CP_B)$ 67.7 Hz, of doublets, $^1J(CRh)$ 16.1 Hz, of quartets, $^2J(CP_A)$ 13.7 Hz. Coalescence of the distinct phosphine resonances and loss of rhodium coupling in both ^1H and ^{31}P spectra along with loss of phosphorus coupling from the proton resonance of the methyl group at $+65\,^\circ C$ all indicate intermolecular exchange. In the analogous cobalt compound, $(Me_3P)_4CoMe$, the methyl resonance in the ^1H NMR spectrum is a quartet at $-80\,^\circ C$ (coupling to the axial phosphine is not resolved) and at $-30\,^\circ C$ and above the resonance is a binomial quintet, behavior that is consistent with intramolecular exchange [14]. For the analogous iridium complex, $(Me_3P)_4Ir(Me)$, the methyl resonance in the ^1H NMR spectrum is a binomial quintet and the iridium compound, like the cobalt compound, exhibits intramolecular phosphine site exchange at least at room temperature [15]. This observation is consistent with results for five-coordinate rhodium and iridium diene compounds, in which rhodium complexes tend to dissociate phosphine ligands at room temperature or below whereas iridium complexes undergo intramolecular fluxional processes and do not dissociate ligands until higher temperatures are reached [2,16]. The origin of the changes in bond strength upon descending a column in the periodic table has been rationalized for six, five, and four-coordinate complexes by Ziegler [17]. These ideas can be applied to the phosphine alkyls of Co, Rh, and Ir in order to explain the trends in fluxionality.

Heating $(Me_3P)_4Rh(Me)$ for several hours in aromatic hydrocarbons solvents does not result in arene activation. Heating $(Me_3P)_3Rh(Me)$ in C_6H_6 at $70\,^\circ C$ for several hours gives methane (^1H NMR) and $(Me_3P)_3RhPh$ (^1H and $^{31}P\{^1H\}$ NMR). Using toluene as solvent, $(Me_3P)_3Rh(o\text{-tolyl})$, $(Me_3P)_3Rh(m\text{-tolyl})$, and $(Me_3P)_3Rh(p\text{-tolyl})$ are formed (^1H and $^{31}P\{^1H\}$ NMR) in a ratio of 0.28/2.14/1.00, respectively, along with methane (^1H NMR). Using $(Me_3P)_3Rh(Me)$ and toluene-d_8 gives CH_3D, observed in ^1H NMR spectrum as a 1/1/1 triplet at δ 0.20. We have followed the reactions in toluene and toluene-d_8 by NMR spectroscopy as a function of time. The rates do not follow pseudo-first order kinetics over three half-lives, but they level off with time. Accordingly, all we can measure is the initial rate constants of 4.6×10^{-5} s^{-1} for C_7H_8 and 2.8×10^{-5} s^{-1} for C_7D_8.

Heating the individually prepared *ortho-*, *meta,* and *para*-tolyl compounds in C_7D_8 at $70\,^\circ C$ for 11 h does not lead to isomerization nor to further arene activation of solvent by the aryl compounds. The distribution of isomers is therefore kinetically determined. The *meta-* to *para*-tolyl ratio is close to statistical and the small amount of the *ortho*-tolyl isomer may be due to steric congestion in the transition state. These results are consistent with a mechanism in which the arene first forms an η^2-complex, with the arene and two phosphine ligands on equatorial sites in a trigonal bipyramid. Related trigonal bipyramidal geometries have been determines for $(Me_3P)_3Rh(Me)(C_2H_4)$ by NMR spectroscopy and $(Me_3P)_3Rh(Me)(C_2F_4)$ by X-ray crystallography in which the olefin is in the equatorial site [18]. Oxidative additions of the arene C–H bond followed by reductive elimination of methane will give the aryl compounds in a process similar to that which has been studied in detail by Jones and Feher [19].

Heating the benzyl compound at $70\,^\circ C$ for 20 h in either C_7D_8 or C_7H_8 gives a clean conversion to $(Me_3P)_3Rh(o\text{-tolyl})$. A yield of 80% can be estimated on the basis of the NMR spectrum; the only other compound observed is starting material. No CH(D) activation of solvent is observed. Although the η^3-benzyl compound

rearranges to the *o*-tolyl compound, the isomerization is slower than the C–H activation by $(Me_3P)_3Rh(Me)$ so detectable amounts of the benzyl species should have been seen during the course of the activation experiments; none were. The rearrangement of $(Et_3P)_3Ir$(benzyl) to $(Et_3P)_3Ir$(o-tolyl) has been mentioned briefly [12b].

In the course of the arene activation experiments the $^{31}P\{^1H\}$ NMR spectra always contain a set of lines which appear to be the A_2B portion of an A_2BX spin system. In the reaction of $(Me_3P)_3Rh(Me)$ with toluene the maximum extent of these resonances is ca. 5% of the total phosphorus signal intensity. When $(Me_3P)_3Rh(Me)$ is heated at 70 °C in perdeuteromethylcyclohexane three sets of $^{31}P\{^1H\}$ NMR resonances are observed, in addition to starting material which is the major product after eleven hours. These resonances are the A_3BX pattern of $(Me_3P)_4Rh(Me)$, a doublet resonance which we have not identified, and a A_2BX set of resonances. We have identified the compound responsible for the A_2BX set of resonances as $(Me_3P)_3Rh(C_2H_4)Me$, prepared by independent synthesis [18], in which ethylene and two trimethylphosphine ligands occupy the equatorial sites of a trigonal bipyramidal complex. The ethylene is not formed from the Me–Rh group since heating $(Me_3P)_3RhCD_3$ in methylcyclohexane and examining the $^2H\{^1H\}$ NMR spectrum shows no incorporation of deuterium into the ethylene resonances but it does show deuterium incorporation into the phosphine methyl resonances. The low yield and unselective nature of the reaction has precluded further study.

In conclusion, we do not know whether the compound originally described as $(Me_3P)_3Rh$(*m*-tolyl) [4] is the isomerically pure compound since the NMR spectra are more complex than originally reported, nor can we conclude which set of the reactions depicted in eq. 5, 6, and 7 or in eq. 8 is the best description of the reactions. We have, however, shown that $(Me_3P)_3Rh(Me)$ activates arene C–H bonds, albeit poorly.

Experimental

All manipulations were done as previously described, including the arene activation experiments [2]. The $^{31}P\{^1H\}$ NMR spectra are in Table 1.

$(PMe_3)_3RhCl$. A modification of the published procedure was employed [20]. Trimethylphosphine (2.0 ml, 21 mmol) was added to a THF solution (125 ml) of $[(\mu\text{-Cl})Rh(COD)]_2$ (1.38 g, 2.80 mmol). A yellow precipitate formed immediately. The mixture was heated to reflux under a slow stream of argon. After 14 h the mixture had become a homogeneous orange solution. The solvent was removed under reduced pressure and the orange-red residue was extracted with toluene. Cooling the filtered toluene solution to −70 °C yielded dark orange (nearly red) crystals of $(PMe_3)_3RhCl$ (1.36 g, 66.0%). ^1H and $^{31}P\{^1H\}$ NMR spectra were consistent with those originally reported [20].

$[(PMe_3)_4Rh]Cl$. The cationic complex was prepared by modifying a literature procedure [21]. Trimethylphosphine (2.5 ml, 26 mmol) was added to a THF solution (80 ml) of $[(\mu\text{-Cl})Rh(COD)]_2$ (1.28 g, 2.60 mmol). Yellow material precipitated immediately. The Schlenk tube was sealed and heated to 80 °C. After 15 min all of the precipitate dissolved to produce a red solution. Slow cooling of the solution to room temperature yielded red blocks (2.19 g, 95.2%) of $[(PMe_3)_4Rh]Cl$.

$(PMe_3)_3RhMe$. This compound was prepared by a variation on the procedure of a published recipe [4]. Trimethylphosphine (0.60 ml, 6.3 mmol) was added to a toluene solution (50 ml) of $[(\mu\text{-Cl})Rh(COD)]_2$ (506 mg, 1.03 mmol) at room temperature. The golden solution immediately became orange. After 2 h the mixture was cooled to $-70\,^\circ C$, and some of the orange $(PMe_3)_3RhCl$ which had formed now precipitated. A diethyl ether solution (1.4 ml) of MeLi (1.6 *M*, 2.2 mmol) was added to the suspension at $-70\,^\circ C$, and the mixture was allowed to warm to $-5\,^\circ C$ over 3 h. The solvent was removed under reduced pressure, and the orange residue was extracted with pentane. The extract was filtered, concentrated, and cooled to $-70\,^\circ C$ to yield orange crystals (495 mg, 69.5%) of $(PMe_3)_3RhMe$:

^1H NMR ($-20\,^\circ C$, toluene-d_8, 202 MHz) δ 1.17 (br s, 18H, PMe_3), 1.15 (d, overlapping with peak at δ 1.17, ^2J(H–P ~ 6 Hz, 9H, PMe_3), 0.19 (tdd, ^3J(H–P) 8.6 Hz, ^3J(H–P) 5.5 Hz, ^2J(H–Rh) 1.8 Hz, 3H, Rh–Me). The $(PMe_3)_3RhCD$ was prepared similarly using $LiCD_3$. $^{31}P\{^1H\}$ NMR ($-40\,^\circ C$, methylcyclohexane, 82 MHz) δ −10.40 (dd, ^1J(P–Rh 154.0 Hz, ^2J(P–P) 36.1 Hz, 2P), −15.71 (dt, ^1J(P–Rh) 122.7 Hz, ^2J(P–P) 36.1 Hz, 1P); $^2H\{^1H\}$ NMR ($-40\,^\circ C$, methylcyclohexane, 31 MHz) δ −0.02 (br s, CD_3,).

$(PMe_3)_3RhCH_2CMe_3$. A Schlenk tube was charged with $(PMe_3)_3RhCl$ (300 mg, 0.818 mmol) and $LiCH_2CMe_3$ (68 mg, 0.87 mmol). Under vacuum, 50 ml of toluene was distilled and frozen onto the reactants directly from sodium benzophenone. After closing off the reaction vessel, the toluene was melted by immersion of the apparatus in a dry ice/alcohol bath. The reaction mixture was stirred for 3 h as the dry ice bath was allowed to reach room temperature. After stirring for another 18 h, the solvent was removed under reduced pressure to yield a red-orange residue. A pentane extract of the residue was filtered, concentrated and cooled slowly to $-70\,^\circ C$ to produce orange blocks (150 mg, 45.6%) of $(PMe_3)_3RhCH_2CMe_3$ which melted at room temperature; satisfactory elemental analysis could not be obtained: ^1H NMR ($20\,^\circ C$, toluene-d_8, 500 MHz) δ 1.44 (s, 9H, CMe_3), 1.21 (virt t of d, $|^2J(H–P) + {}^4J(H–P|$ = 4.7 Hz, ^3J(H–Rh) 1.2 Hz, 18H, PMe_3), 1.15 (tdd, ^3J(H–P) 11.2 Hz, ^3J(H–P) 4.8 Hz, ^2J(H–Rh) 1.4 Hz, 2H, CH_2), 1.08 (d, ^2J(H–P) 5.5 Hz, 9H, PMe_3); $^{13}C\{^1H\}$ NMR (22 °C, toluene-d_8, 126 MHz) δ 38.09 (s, 1C, CMe_3), 36.62 (d, ^3J(C–Rh) 3.8 Hz, 3C, CMe_3), 29.82 (ddt, ^2J(C–P) 70.7 Hz, ^1J(C–Rh) 23.8 Hz, ^2J(C–P) 11.7 Hz, 1C, CH_2), 22.49 (dt, ^1J(C–P) 15.8 Hz, ^3J(C–P) 4.0 Hz, 3C, PMe_3), 20.62 (overlapping with solvent, 6C, PMe_3).

$(PMe_3)_3Rh(\eta^3\text{-}CH_2Ph)$. A fresh diethyl ether solution (25 ml) of $PhCH_2Li \cdot 1.2\ Et_2O$ (127 mg, 0.680 mmol) [22] was added to a toluene suspension (50 ml) of $[(PMe_3)_4Rh]Cl$ (275 mg, 0.621 mmol) at $-70\,^\circ C$. The reaction mixture was gradually allowed to warm to room temperature, and the solution was stirred for a total of 16 h. Within the first 2 h the color became red. The solvent was removed under reduced pressure, and the red residue was extracted with pentane. After filtration and concentration, the extract was cooled slowly to $-70\,^\circ C$ to produce a gelatinous, yellow material. The mother liquor was filtered, concentrated and cooled again to yield deep red (nearly black) crystals (129 mg, 49.2%) of $(PMe_3)_3Rh(\eta^3\text{-}CH_2Ph)$: ^1H NMR ($-50\,^\circ C$, THF-d_8, 202 MHz) δ 6.61 (m, 3H, aryl H), 6.42 (m, 2H, aryl H), 1.69 (td, ^3J(H–P) 8.6 Hz, ^3J(H–P) 6.6 Hz, 2H, CH_2Ph), 1.26 (virt t of d), $|^2J(H–P + {}^4J(H–P|$ = 4.7 Hz, ^3J(H–Rh) 1.2 Hz, 18 H, PMe_3), 1.01 (d, ^2J(H–P) 7.1 Hz, 9H, PMe_3); $^{13}C\{^1H\}$ NMR ($-51\,^\circ C$, THF-d_8, 126 MHz) δ 122.64 (d, ^2J(C–P) 45.0 Hz, 2C, *ortho* C), 120.36 (dm, ^2J(C–P) 47.8 Hz, 1C, *ipso* C), 199.63 (d, ^3J(C–P)

39.8 Hz, 2C, *meta* C), 118.13 (d, ^4J(C–P) 5.6 Hz, 1C, *para* C), 26.40 (ddt, ^2J(C–P) 45.7 Hz, ^1J(C–Rh) 13.2 Hz, ^2J(C–P) 6.5 Hz, 1C, CH_2), 23.21 (virt t, $|^1J(C-P) + {}^3J(C-P)| = 18.7$ Hz, 6C, PMe_3), 20.89 (dt, ^1J(C–P) 19.6 Hz, ^3J(C–P) 4.9 Hz, 3C, PMe_3; mass spectrum (70 eV) m/z 422 $(M)^+$. Anal. Found: C, 45.3; H, 8.15; P, 19.1. $C_{16}H_{34}P_3Rh$ calcd.: C, 45.5; H, 8.13; P, 22.0%.

$(PMe_3)_3RhPh$. Trimethylphosphine (0.27 ml, 2.8 mmol) was added to a toluene solution (50 ml) of $[(\mu\text{-Cl})Rh(COD)]_2$ (317 mg, 0.643 mmol) at −70 °C. A yellow-white precipitate formed. After 10 min phenyllithium (165 mg, 1.96 mmol) was added. After 10 additional min the bright, light yellow mixture was removed from the cooling bath. As the mixture warmed to room temperature it became homogeneous, and the color became red-orange. The solvent was removed under reduced pressure. A pentane extract of the residue was filtered, concentrated, and cooled to −70 °C to produce a mixture of dark red needles of $(COD)Rh(PMe_3)Ph$ and orange blocks of $(PMe_3)_3RhPh$ which were manually separated: ^{1}H NMR (20 °C, C_6D_6, 500 MHz) δ 7.89 (tm, ^3J(H–H) 5.2 Hz, 2H *ortho* H), 7.21 (t, ^3J(H–H) 7.0 Hz, 2H, *meta* H), 7.06 (tm, ^3J(H–H) 7.2 Hz, 1H, *para* H), 1.11 (d, ^2J(H–P) 5.1 Hz, 9H, PMe_3), 0.98 (virt t of d, $|^2J(H-P) + {}^4J(H-P)| = 4.9$ Hz. ^3J(H–Rh) 1.3 Hz, 18H, PMe_3); $^{13}C\{^1H\}$ NMR (20 °C, C_6D_6, 126 MHz) δ 141.01 (s, 2C, *ortho* C), 125.74 (s, 2C, *meta* C), 120.81 (s, 1C, *para* C), 22.83 (dm, ^1J(C–P) 16.6 Hz, 3C, PMe_3), 19.46 (virt t, $|^1J(C-P) + {}^3J(C-P)| = 23.0$ Hz, 6C, PMe_3.

$(PMe_3)_3Rh(p\text{-}tolyl)$. A freshly prepared THF solution (10 mL) of (*p*-tolyl)Li · 0.5 Et_2O (175 mg, 1.29 mmol) [22] was added to a toluene suspension (70 ml) of $[(PMe_3)_4Rh]Cl$ (350 mg, 0.791 mmol) at −70 °C. The reaction mixture was allowed to warm to room temperature, and the solution was stirred overnight. After removal of the solvent under reduced pressure, the orange residue was extracted with pentane. Filtration, concentration, and slow cooling of the extract to −70 °C yielded golden, needle-shaped crystals of $(PMe_3)_3Rh$(*p*-tolyl): ^{1}H NMR (20 °C, toluene-d_8, 202 MHz) δ 7.65 (m, 2H, *ortho* H), 6.99 (br d, ^3J(H–H) 7.1 Hz, 2H, *meta* H), 2.31 (s, 3H, tolyl CH_3), 1.13 (d, ^2J(H–P) 4.4 Hz, PMe_3), 0.98 (br m, 18H, PMe_3); $^{13}C\{^1H\}$ NMR (20 °C, toluene-d_8, 126 MHz) δ 140.73 (dm, ^2J(C–Rh) 29.4 Hz, 2C, *ortho* C), 126.84 (m, 2C, *meta* C), 22.96 (dm, ^1J(C–P) 16.3 Hz, 3C, PMe_3), 21.42 (s, 1C, tolyl CH_3), 19.50 (virt t of m, $|^1J(C-P) + {}^3J(C-P)| = 22.4$ Hz, 6C, PMe_3), the *ipso* and *para* carbons were not observed; mass spectrum (70 eV) m/z 422 $(M)^+$. Anal. Found: C, 45.8; H, 8.47; P, 21.2. $C_{16}H_{34}P_3Rh$ calcd.: C, 45.5; H, .13; P, 22.0%.

$(PMe_3)_3Rh(m\text{-}tolyl)$. A THF solution (10mL) of *m*-tolyllithium (216 mg, 2.20 mmol) [23] was added to a toluene suspension (75 ml) of $[(PMe_3)_4Rh]Cl$ (500 mg 1.13 mmol) at −70 °C. The reaction mixture was allowed to reach room temperature and was stirred for 20 h. The solvent was removed under reduced pressure, and the product was crystallized from pentane as described above. Yield was 397 mg (83.2%) of orange crystals: ^{1}H NMR (22 °C, toluene-d_8, 500 MHz) δ 7.62 (br s, 1H, *ortho* H), 7.56 (m, 1H, *ortho* H), 7.06 (t, ^3J(H–H) 7.3 Hz, 1H, *meta* H), 6.80 (d, ^3j(H–H) 7.2 Hz, 1H, *para* H), 2.34 (s, 3H, tolyl CH_30, 1.13 (d, ^2J(H–P) 4.8 Hz, 9H, PMe_3), 0.98 (br s, 18H, PMe_3); mass spectrum (70 eV) m/z 422 $(M)^+$. Anal. Found: C, 45.4; H, 8.29; P, 19.3. $C_{16}H_{34}P_3Rh$ calcd.: C, 45.5; H, 8.13; P, 22.0%.

$(PMe_3)_3Rh(o\text{-}tolyl)$. A freshly prepared THF solution (20 mL) of *o*-tolyllithium (145 mg, 1.48 mmol) [23] was added to a toluene suspension (50 ml) of $[(PMe_3)_4Rh]Cl$ (350 mg, 0.791 mmol) at −70 °C. The mixture was allowed to warm

gradually to room temperature and was stirred for 16 h. The solvent was removed under reduced pressure. A pentane extract of the yellow-orange residue was filtered, concentrated, and slowly cooled to −70 °C to yield 179 mg (53.6%) of red-orange, crystalline $(PMe_3)_3Rh(o\text{-tolyl})$: ^1H NMR (25 °C, C_6D_6, 500 MHz) δ 7.71 (br t, ^3J(H–H) 6.0 Hz, 1H, *ortho* H), 7.16 (br d, ^3J(H–H) 6.8 Hz, 1H, *meta* H), 7.07 (m, 2H, *meta* H and *para* H), 2.75 (s, 3H, tolyl CH_3), 1.06 (d, ^2J(H–H) 5.1 Hz, 9H, PMe_3), 0.90 (virt t of d, $|^2J(H-P) + {}^4J(H-P)| = 5.1$ Hz, ^3J(H–Rh) 1.1 Hz, 18H, PMe_3); $^{13}C\{^1H\}$ NMR (25 °C, C_6D_6, 126 MHz) δ 145.59 (s, 1C, *ortho* C), 140.23 (m, 1C, *ortho* C), 126.68 (m, 1C, *meta* C), 122.88 (m, 1C, *meta* C), 120.97 (s, 1C, *para* C), 28.07 (s 1C, tolyl CH_3), 22.47 (dm ^1J(C–P 17.3 Hz, 3C, PMe_3), 19.50 (virt t of m, $|^1J(C-P) + {}^3J(C-P)| = 24.7$ Hz, 6C, PMe_3), the *ipso* carbon was not observed; mass spectrum (70 eV) *m/z* 422 $(M)^+$. Anal. Found: C, 45.5; H, 8.33; P, 19.2. $C_{16}H_{34}P_3Rh$ calcd.: C, 45.5; H, 8.13; P, 22.0%.

$(PMe_3)_4RhMe$. Trimethylphosphine (1.1 ml, 11.6 mmol) was added to a toluene solution (80 ml) of $[(\mu\text{-Cl})Rh(COD)]_2$ (701 mg, 1.42 mmol) at room temperature. The originally yellow solution immediately became an orange suspension. After 2 h the mixture was cooled to −65 °C, and 2.0 ml of a diethyl ether solution of MeLi (1.6 *M*, 3.2 mmol) was added. Within 3 h the reaction mixture was allowed to warm to −10 °C. At this point the orange slurry had become a pale yellow solution. Stirring was continued for another hour as the cooling bath reached 0 °C. At this temperature the solvent was removed under reduced pressure. A pentane extract of the yellow residue was filtered, concentrated to a volume of 5–10 ml, and cooled slowly to −70 °C to yield yellow blocks (550 mg, 41.7%) of $(PMe_3)_4RhMe$: ^1H NMR (−65 °C, toluene-d_8, 202 MHz) δ 1.21 (br s, 27 H, PMe_3), 1.11 (d, ^2J(H–P 6.3 Hz, 9H, PMe_3), 0.05 qdd, ^3J(H–P) 11.5 Hz, ^3J(H–P) 4.2 Hz, ^2J(H–Rh) 1.3 Hz, 3H, Rh–Me); $^{13}C\{^1H\}$ NMR (−61 °C, toluene-d_8, 126 MHz) δ 25.77 (dq, ^1J(C–P) 19.1 Hz, ^3J(C–P) 8.1 Hz, 3C, PMe_3), 22.87 (m, 9C, PMe_3), −8.33 (ddq, ^2J(C–P) 67.7 Hz, ^1J(C–Rh) 16.1 Hz, ^2J(C–P) 13.7 Hz, 1C, Rh–Me); $^{31}P\{^1H\}$ NMR (−50 °C, toluene-d_8, 82 MHz) δ +1.69 (dq, ^1J(P–Rh) 105.9 Hz, ^2J(P–P) 40.6 Hz, 1P), −23.43 (dd, ^1J(P–Rh) 157.7 Hz, ^1J(P–Rh) 157.7 Hz, ^2J(P–P) 40.6 Hz, 3P); mass spectrum (CI with methane) *m/z* 422 $(M)^+$. Anal. Found: C, 37.6; H, 9.60; P, 27.9. $C_{13}H_{39}P_4Rh$ calcd.: C, 37.0; H, 9.33; P, 29.3%. These were the best analytical results obtained after two attempts.

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