Journal of Organometallic Chemistry, 393 (1990) 287–298
Elsevier Sequoia S.A., Lausanne
JOM 20916

Dichloromethane addition to rhodium-β-diketonate complexes of diphosphines and pyridyl-substituted diphosphines

Paul J. Fennis, Peter H.M. Budzelaar *, John H.G. Frijns

Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B.V.), Postbus 3003, 1003 AA Amsterdam (The Netherlands)

and A. Guy Orpen

School of Chemistry, The University of Bristol, Cantock's Close, Bristol BS8 1TS (U.K.)

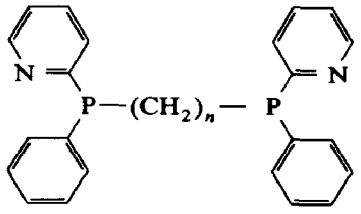
(Received February 28th, 1990)

Abstract

In the reactions of the pyridyldiphosphine ligands $(C_6H_5)(C_5H_4N)P(CH_2)_n$-$P(C_6H_5)(C_5H_4N)$ ($n = 1$, DPyPM; $n = 2$, DPyPE; $n = 3$, DPyPP) with (β-diketonate)Rh(COD), only the phosphorus atoms coordinate to rhodium. The DPyPE and DPyPP complexes react with dichloromethane to give eventually pyridyl-ylid complexes [(β-diketonate)Rh(Cl){$(CH_2NC_5H_4)(C_6H_5)P(CH_2)_nP(C_6H_5)(C_5H_4N)$}]Cl. The (chloro)(chloromethyl) complexes thought to be intermediates can be isolated if aryl-diphosphines $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ are used in the reaction. The structure of the pyridyl-ylid complex [(dipivaloylmethanate)Rh(Cl)(CH_2DPyPE)]Cl has been determined by X-ray diffraction. The rhodium atom is octahedrally surrounded by the two oxygen atoms of the β-diketonate, one axial chlorine, and one axial phosphorus atom (that bearing the pyridyl-ylid group), and the remaining phosphorus atom and the methylene group in the equatorial positions. The ylidic C–N bond is rather long (1.510(4) Å).

Introduction

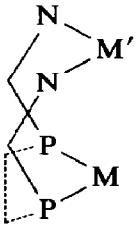
We previously described the synthesis of a series of pyridyl-substituted diphosphines: DPyPM, DPyPE and DPyPP [1]. These phosphines were found to react



($n = 1$: DPyPM; $n = 2$: DPyPE; $n = 3$: DPyPP)

0022-328X/90/$03.50

with $[Rh(CO)_2Cl]_2$ to give homobimetallic complexes. It was expected that the *meso-forms* of DPyPE and DPyPP would be especially useful for the construction of heterobimetallic complexes having a late transition metal M coordinated to the soft phosphorus donors and an early transition metal or main-group metal M′ bound to the hard pyridyl nitrogens, as shown in structure I.



(I)

We decided to bind the late transition metal first, using two (β-diketonate)rhodium(1,5-cyclooctadiene) compounds (A)Rh(COD) as starting materials (A = 2,4-pentanedionate (acetylacetonate, acac) or 2,2,6,6-tetramethyl-heptanedionate (dipivaloylmethanate, dpm)) [2]. As expected, these compounds readily react with our pyridyl-diphosphines to give mononuclear complexes in which only the phosphorus atoms are coordinated to rhodium. These (β-diketonate)Rh(pyridyldiphosphine) compounds should be convenient starting materials for the preparation of heterobimetallic complexes, and we will consider this in a future publication. The mononuclear rhodium compounds are, however, more reactive than we had expected. The present paper deals with the formation of the complexes and one aspect of their reactivity, namely the oxidative addition of dichloromethane and the subsequent intramolecular quaternization of the intermediate chloromethyl complexes. Some (β-diketonate)Rh(diphosphine) complexes of the phenyl-diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 1$, DPPM; $n = 2$, DPPE; $n = 3$, DPPP) were included for comparison.

Results and Discussion

Reactions of diphosphines with (β-diketonate)Rh(COD) and CH_2Cl_2

The 1,5-COD ligand in (A)Rh(COD) (A = acac or dpm) is readily replaced by diphosphine ligands L_2, to give complexes of the type (A)Rh(L_2) as the final products [3]. The NMR data for these complexes are listed in Tables 1 (^{31}P) and 2 (^{13}C). The compounds show a large ^1J(RhP) (≈ 190 Hz), characteristic of Rh^I complexes.

Reactivity studies of (β-diketonate)rhodium-bis(phosphine) complexes are scarce; even the simplest (A)RhL_2 complex, (acac)Rh(PPh_3)$_2$, has not been studied extensively. It has been reported to undergo oxidative addition with a number of reactive substrates (MeI, C_3F_7I, $(CF_3)_2CO$, etc.) [4]. We observed that the diphosphine complexes also add the much less reactive dichloromethane, to give stable chloromethyl complexes (A)Rh(Cl)(CH_2Cl)(L_2) (Scheme 1) [5]. In most cases a mixture of the symmetric and asymmetric isomers is obtained. The product ratio depends on both the β-diketonate and the diphosphine: long diphosphine chain lengths and bulky β-diketonate groups appear to promote the formation of the symmetrical isomer. Inspection of molecular models suggests that there is steric interaction

Table 1

^{31}P NMR data for (A)Rh(L_2) complexes: δ_P, ppm (^1J(RhP); ^2J(PP) [a], Hz)

L_2	acac	dpm
DPPM	−19.5(164)	−18.5(164)
DPPE	70.0(194;51)	72.1(194;52)
DPPP	37.3(182)	38.1(182)
DPyPM [b]	[c]	−16.2(159)
DPyPE [b]	73.8(188;49)	75.2(189;48)
DPyPP [b]	38.9(178;73)	39.9(178;75)
2 Me_2PPy	[c]	27.7(186)

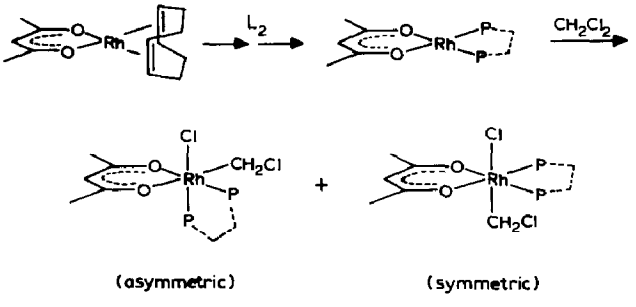
[a] Determined from the ^{13}C spectrum. [b] Mixtures of *rac* and *meso* isomers; data given for the major isomer only. [c] Not prepared.

Table 2

^{13}C NMR data for (A)Rh(L_2) complexes

A	L_2	β-diketonate δ_C, ppm (J(RhC), Hz)		diphosphine δ_C, ppm (J(PC), Hz)	
		C=O	CH	P-CH_2	C-CH_2-C
acac	DPPM	185.0	99.6(2)	47.4(23)	
	DPPE	185.0	99.7(3)	28.0(50 [a,e])	
	DPPP	184.6	99.5(2)	28.7(40 [b,d])	20.5(3)
	DPyPE [c]	185.2	99.9(2)	27.1(54 [a,d])	
	DPyPP [c]	184.7(1)	99.8(3)	27.0(41 [b,d])	21.1(5 [d])
dpm	DPPM	194.3	89.6(2)	46.4(23)	
	DPPE	194.3	89.9(2)	28.3(50 [a,e])	
	DPPP	194.0	89.7(2)	29.2(37 [b,d])	20.6(3 [d])
	DPyPM [c]	194.4(1)	89.9(2)	43.7(26)	
	DPyPE [c]	194.6(1)	90.0(2)	27.5(53 [a,e])	
	DPyPP [c]	194.3(2)	89.9(2)	27.3(41 [b,d])	20.6(3 [d])
	2 Me_2PPy	194.3(1)	90.4(4)		

[a] $|^1J(PC)+{}^2J(PC)|$. [b] $|^1J(PC)+{}^3J(PC)|$. [c] Mixture of *rac* and *meso* isomers; data given for the major isomer only. [d] J(RhC) = 2 Hz. [e] J(RhC) = 4 Hz.



A	L_2	ratio *as/s*
acac	DPPM	4
	DPPE	6
	DPPP	0.25
dpm	DPPM	2.5
	DPPE	3
	DPPP	< 0.1

Scheme 1. Reaction of (A)Rh(COD) with diphosphines and CH_2Cl_2.

Table 3

^{31}P NMR data for (A)Rh(Cl)(CH_2Cl)(L_2) complexes: δ_P, ppm (^1J(RhP), Hz)

A	L_2	Asymmetric			Symmetric
		P_{eq} [a]	P_{ax}	^2J(PP) (Hz)	
acac	DPPM	−18.8(118)	−11.0(124)	84	−12.9(117)
	DPPE	58.6(137)	61.8(147)	17	51.5(137)
	DPPP	19.0(126)	22.2(134)	40	24.2(127)
dpm	DPPM	−17.5(117)	−11.6(126)	85	−11.7(117)
	DPPE	55.2(136)	59.2(148)	19	53.4(137)
	DPPP	18.1(126)	20.7(138)	40	24.3(129) [b]

[a] Assignment based on similarity of ^1J(RhP) with that of the symmetric (eq, eq) isomer. [b] J(PP) = 56 Hz, determined from the ^{13}C spectrum.

Table 4

^{13}C NMR data for (A)Rh(Cl)(CH_2Cl)(L_2) complexes

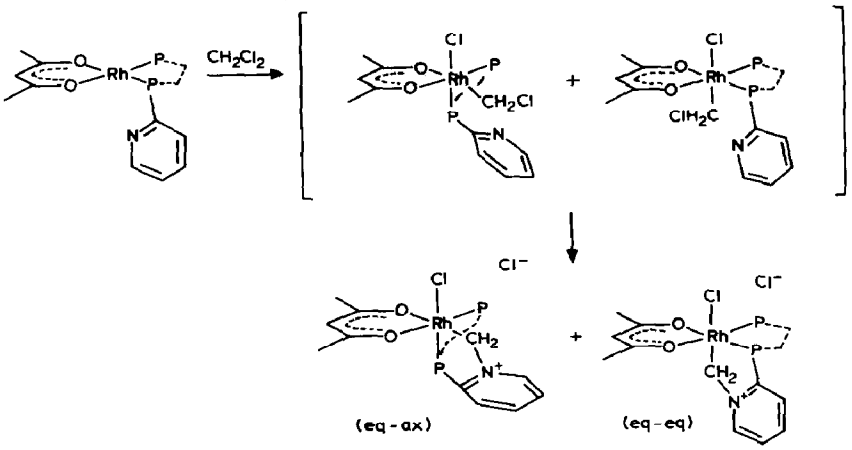
A	L_2	β-diketonate δ_C, ppm (J(RhC), Hz)		diphosphine δ_C, ppm (J(PC) Hz)		CH_2Cl δ_C(J(RhC); J(PC) Hz)
		C=O	CH	P–CH_2	C–CH_2–C	
acac	DPPM [a]	187.0, 185.0(3)	98.3	38.3(26 [e])		43.6(29;11,6)
	DPPE [a]	186.4, 185.2(2)	98.6(2)	23.0(35,9 [c]), 23.2(35,9 [c])		44.4(23;11,6)
	DPPP [b]	184.7(1 [f])	98.4(2)	26.5(37)	19.6(–)	50.3(29;8)
dpm	DPPM [a]	197.0, 194.9(4)	89.2(1)	36.3(26 [e])		43.7(28;11,7)
	DPPE [a]	196.7, 195.2(2)	90.4(1)	22.3(36,9 [d]) 26.8(34,11 [d])		44.9(27;10,6)
	DPPP [b]	193.6(1 [f])	88.9(2)	27.8(37)	19.8(–)	49.5(29;7)

[a] Asymmetric isomer. [b] Symmetric isomer. [c] J(RhC) = 1 Hz. [d] J(RhC) = 2 Hz. [e] Average J(PC). [f] ^3J(PC) = 2 hz.

between one phenyl group of the equatorial phosphorus atom and one alkyl group of the β-diketonate, and that this interaction increases with the increasing bite angle of the diphosphine. Thus, the variations in the observed product ratios may be primarily due to steric factors. The oxidative-addition products have small ^1J(RhP) coupling constants (≈ 130 Hz), characteristic of Rh^{III} complexes. NMR data for the chloromethyl complexes are given in Tables 3 (^{31}P) and 4 (^{13}C).

Reactions of pyridyl-substituted diphosphines with (β-diketonate)Rh(COD) and CH_2Cl_2

(A)Rh(COD) reacts rapidly with phosphines, but not with hard bases such as 2,2′-bipyridine or o-phenanthroline. Thus it is not surprising that reactions with pyridyl-substituted diphosphines give exclusively *P*-coordinated pyridyl-diphosphine complexes; NMR data are included in Tables 1 and 2. The reactions of these pyridyldiphosphine complexes with dichloromethane are both more rapid and more complicated than those of the normal diphosphine complexes. The initially formed chloromethyl addition product is not observed, because it immediately reacts further in this case to give a pyridyl-ylid complex, as illustrated in Scheme 2. The starting



Scheme 2. CH_2Cl_2 addition and intramolecular quaternization of (A)Rh(pyridyl-diphosphine) complexes.

pyridyldiphosphines are all mixtures of *rac* and *meso* forms [1]. For L_2 = DPyPE, each of these diastereomers gives rise to only one pyridyl-ylid complex. The dpm derivative was shown by X-ray diffraction to have one axial and one equatorial phosphorus atom (with respect to the plane of the diketonate ligand); the axial phosphorus atom carried the pyridyl-ylid group. This structure is thus closely related to that of the dominant isomer of (A)Rh(Cl)(CH_2Cl)(DPPE) (vide supra), and this suggests that the stereochemistry of the dichloromethane adduct is preserved during the quaternization reaction [5]. For L_2 = DPyPM, the reaction with dichloromethane gave a complex mixture of products from which no pyridyl-ylid complex could be isolated. For L_2 = DPyPP, the reaction with CH_2Cl_2 produced (for each diastereomer of the ligand) a mixture of two isomeric ylid complexes, for which we propose the structures shown in Scheme 2 (i.e., the eq–eq and eq–ax arrangements). This assignment is based on the assumptions that the initial dichloromethane addition to (A)Rh(DPyPP) gives products analogous to those of (A)Rh(DPPP) and that subsequent quaternization proceeds with retention of stereochemistry.

The NMR data for the pyridyl-ylid complexes are listed in Tables 5 and 6. The phosphorus atom carrying the pyridyl-ylid group (P_{yl}) consistently resonates at lower field than the other phosphorus atom: this low-field shift may be ascribed to a 5-membered chelate-ring effect [6]. It also shows a characteristic broadening which decreases at lower temperature and is best explained in terms of residual coupling to the quadrupolar ylidic nitrogen. The ^{13}C NMR spectra also show broadened lines for the carbon atoms of the ylid ring, and this prevented complete assignment of the pyridyl-ylid ring ^{13}C resonances. Since there are no good reference data for this type of compound, we also prepared the simple model compound (dpm)Rh(Me_2PPy)$_2$ and the product of its reaction with CH_2Cl_2. The ^{13}C spectrum of this pyridyl-ylid could be interpreted without difficulty and helped in locating and assigning many of the broadened ylid ring resonances in the other complexes.

The presence of both a normal pyridyl group and a pyridyl-ylid group in the quaternized product allows evaluation of the bonding in the ylid group. The substitution shifts for ylid formation are shown together with those for normal

Table 5

^{31}P NMR data for $[(A)Rh(Cl)(CH_2L_2)]^+ Cl^-$ complexes: δ_P, ppm (^1J(RhP), Hz)

A	L_2	P_L	P_{yl} [a]	^2J(PP (Hz)
acac	DPyPE [b]	63.7(122)	90.0(139)	15
		62.9(123)	93.7(135)	14
	DPyPP [b,c]	22.8(116)	60.9(130)	36
		20.4(116)	60.2(131)	37
		23.3(116)	61.0(125)	50
		22.9(118)	60.7(125)	51
dpm	DPyPE [b]	62.9(121)	88.1(140)	16
		62.4(122)	91.2(136)	14
	DPyPP [b]	20.8(116)	59.9(131)	38
		19.5(115)	58.6(131)	38
	2 Me_2PPy	23.8(125)	54.0(131)	46

[a] Assignment based on the broadening of the P_{yl} resonance and on the low-field shift due to the chelate-ring effect. [b] Mixture of *rac* and *meso* isomers; first entry corresponds to most abundant isomer. [c] Entries 1 and 2 are assigned to the (eq,ax)-isomer, and entries 3 and 4 (minor components) to the (eq,eq) isomer (see text); these assignments are based on the observation that ^1J(RhP) is larger for P *trans* to Cl than for P *trans* to O (see Table 3)

quaternization [7] in Fig. 1 below. Comparison of the $\Delta\delta$ values suggests that the ylid complexes are indeed best considered as substituted alkylpyridinium salts [8], although the electron density depletion of the pyridyl ring appears to be somewhat smaller than that in the methylpyridinium ion.

The facile reactions of (A)Rh(diphosphine) with CH_2Cl_2 demonstrate both the high reactivity of $(A)Rh(L_2)$ complexes and the non-innocent nature of the pyridyl

Table 6

^{13}C NMR data for $[(A)Rh(Cl)(CH_2L_2)]Cl$ complexes

(a) Ligand and methylene resonances

A	L_2	β-diketonate (δ_C, ppm (J(RhC),Hz))		diphosphine (δ_C, ppm (J(PC),Hz))	CH_2N (δ_C(J(RhC); J(PC))
		C=O	*C*H	P–*C*H_2	
acac	DPyPE [a]	188.1, 185.6(3)	99.9(1)	21.9(36,9), 26.0(35,8)	65.7(28;10,4)
dpm	DPyPE [a]	197.5, 195.5(3)	90.0	21.5(37.8) (2×)	66.1(26;10,4)
	2 Me_2PPy	194.8, 196.4(3)	89.4		63.5(31;13,13)

(b) Pyridyl and pyridyl-ylid resonances for $[(dpm)Rh(Cl(CH_2PyPMe_2)(PyPMe_2)]Cl$

Carbon	δ_C, ppm (J(PC); J(RhC), Hz)	
	Pyridyl	Pyridyl-ylid
2	155.5(74;2)	155.3(50)
3	125.3(17)	130.9(4)
4	136.6(7)	143.3(4)
5	124.4(3)	128.9
6	149.2(16)	146.3(8)

[a] Mixture of *rac* and *meso* isomers; data given for the major isomer only.

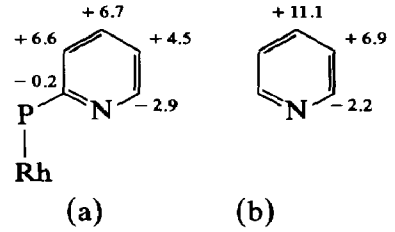
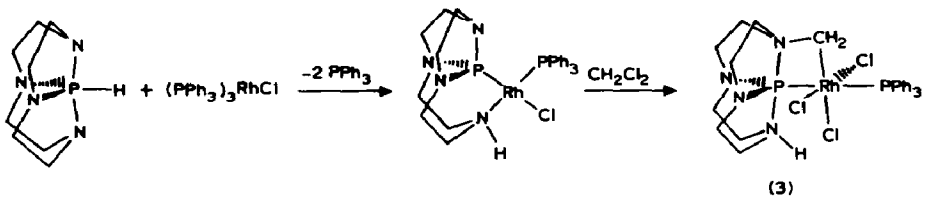


Fig. 1. Influence of quaternization at nitrogen on ^{13}C NMR shifts of pyridines, $\Delta\delta$ (ppm). (a) Differences between ylid and normal pyridyl ring in $[(dpm)Rh(Cl)(PyPMe_2)(CH_2PyPMe_2)]^+$; (b) Differences between pyridine and methylpyridium ion [7].

groups in pyridylphosphine ligands. In particular, the reluctance of (A)Rh(Cl)(CH_2Cl)(diphosphine) to quaternize with external pyridine [5] contrasts strongly with the rapid intramolecular quaternization of (A)Rh(Cl)(CH_2Cl)(pyridyldiphosphine). Many examples of phosphorus-ylid complexes are known, but nitrogen-ylid complexes are much less common. They have been suggested to be intermediates in the reaction of amines with carbene complexes [9,10]; in general, they dissociate readily into carbene complexes and free amine. Platinum pyridyl-ylid complexes have been prepared via the rearrangement of platinacyclobutanes [11]. There are a few reports of nitrogen-ylid formation by nucleophilic substitution. Moss et al. recently prepared several ylid complexes from $CpFe(CO)_2CH_2X$ (X = Cl, Br) and neutral nucleophiles, including trimethylamine and pyridine [12]. Werner found that $(C_5H_5)Rh(PMe_3)(I)(CH_2I)$ reacts with free pyridine to give $[(C_5H_5)Rh(PMe_3)(I)(CH_2NC_5H_5)]^+[I]^-$ (**2**) [8]. Lattman et al. observed CH_2Cl_2 addition and intramolecular quaternization of a rhodium-cyclenphosphorane complex to give the ylid complex **3** [13]. Formation of phosphorus-ylid complexes by nucleophilic substitution is more common [12,14].



X-ray structure of [(dpm)Rh(Cl)(CH_2DPyPE)]Cl · CH_2Cl_2 (1)

The crystal structure of the title complex consists of isolated cations, chloride anions and dichloromethane molecules of crystallization. In the cation (Fig. 2), the rhodium atom is approximately octahedrally surrounded by chloride, chelating dpm, and the DPyPE-ylid ligand that chelates via a nitrogen-ylid carbon atom and two phosphorus atoms; the second DPyPE pyridyl group is not coordinated. The constraints on the coordination geometry imposed by the DPyPE-ylid moiety result in some marked deviations from ideal octahedral coordination: the *trans* angles are 177.4 (P–Rh–O), 173.1 (C–Rh–O) and 169.8° (Cl–Rh–P); the smallest and largest *cis* angles are 83.8 (P–Rh–P) and 95.5° (C–Rh–P), respectively. The β-diketonate

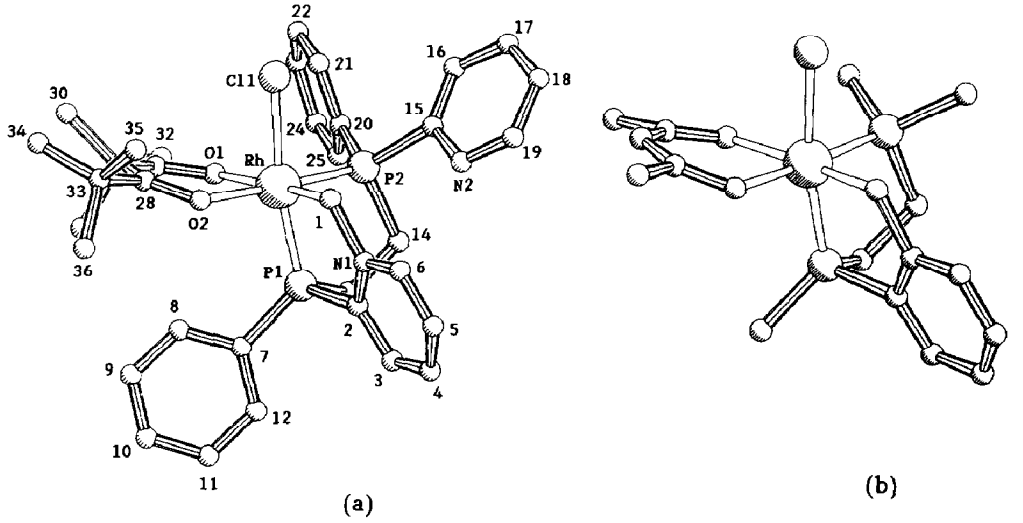


Fig. 2. PLUTO drawing of the (dpm)Rh(Cl)(CH_2-DPyPE)$^+$ cation. Hydrogen atoms are not shown, and in (b) most phenyl, pyridyl and t-butyl carbons have been omitted for clarity as well.

ligand is nearly planar, but its plane makes an angle of 16° with the O–Rh–O plane and is inclined towards the chloride ligand, probably because of steric reasons (the rigid surrounding of P_{yl} forces the phenyl-group bound to it towards the other side of the diketonate plane). The ylidic C–N bond is rather long (1.510(4) Å) compared with those in **2** (1.45(2) Å [8]), **3** (1.49(1) Å [13]) and *N*-alkylpyridinium species (1.46–1.50 Å [15,16]). The rhodium–carbon bond (2.023(3) Å) is nearly identical to that in **3** (2.032(6) Å) but much shorter than that in **2** (2.13(1) Å), which may be due to the *trans* effect of the cyclopentadienyl group in **2**. The *trans* effect of the ylid-substituent is clearly evident from the differences between the two Rh–O bond lengths: 2.093(3) Å (*cis*) and 2.149(2) Å (*trans*).

Conclusions

The ready formation of pyridyl-ylid complexes from chloromethyl complexes illustrates that pyridylphosphines are not innocent ligands and may partake in chemical reactions in the coordination sphere of a metal. It also clearly shows the importance of pre-organization, since the intramolecular presence of a pyridyl group is required for quaternization in the cases we examined.

Supplementary material available. Tables of positional and thermal parameters, bond lengths and angles, and observed and calculated structure factors for compound **1** · CH_2Cl_2 are available from PHMB.

Experimental

All experiments were performed under nitrogen or argon. Solvents were distilled from Na (toluene, hexane) or Na/benzophenone (ether, THF) prior to use; pyridine was distilled from calcium hydride. Commercially available chemicals were used as received. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker WH-250 or Varian XL-200 or VXR-300 instrument. Complexes (acac)Rh(COD) [17] and

(dpm)Rh(COD) [18] were prepared by published methods. The synthesis of the ligands DPyPM, DPyPE and DPyPP has been described before [1].

(β-Diketonate)rhodium(diphosphine) complexes

(A)Rh(COD) (A = acac or dpm) (0.3 mmol) and 0.3 mmol of a diphosphine (DPPM, DPPE, DPPP, DPyPE or DPyPM, DPyPP) or 0.6 mmol of Me_2PPy were dissolved in 10 ml of THF. After 30 min stirring (at 65 °C for DPPE and DPPP), ^{31}P NMR spectroscopy showed that substitution of COD was complete. Removal of the solvent and COD in vacuo gave the yellow (A)Rh(L_2).

Chloro(chloromethyl)complexes

The reaction between (A)Rh(L_2) (L_2 = DPPM, DPPE or DPPP) (0.3 mmol) and dichloromethane (10 ml) was monitored by ^{31}P NMR spectroscopy. During a few days at room temperature the starting material was converted into (A)Rh(Cl)(CH_2Cl)(L_2). Upon completion of the reaction, the solvent and COD are removed in vacuo, leaving the yellow or off-white product.

Table 7

Crystallographic Data for $1 \cdot CH_2Cl_2$

formula	$C_{37}H_{45}Cl_4N_2O_2P_2Rh$
formula weight	856.5
space group	$P\bar{1}$
a, Å	9.175(2)
b, Å	10.236(2)
c, Å	23.398(5)
α, deg	85.33(2)
β, deg	88.72(2)
γ, deg	63.02(2)
V, Å^3	1951.5(6)
Z	2
d_{calc}, g/cm^3	1.46
crystal size, mm	0.5×0.5×0.8
μ (Mo-K_α), cm^{-1}	8.2
orientation reflections, no.; range, °	32; $29 < 2\theta < 30$
scan method	$\theta/2\theta$
data collection range, °	$4 < 2\theta < 50$
decay, %	2
total unique	6877
total observed	5581 ($I > 3\sigma(I)$)
refined parameters	541
transmission factors	0.73 · · · 0.65
R [a]	0.033
R_w [b]	0.0485
g (weights) [c]	0.0005
quality-of-fit [d], S	1.65
residual peaks, e/Å^3	0.74

[a] $R = \Sigma|\Delta|/\Sigma|F_o|$, $\Delta = |F_o| - |F_c|$. [b] $R_w = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$. [c] $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$. [d] $S = [\Sigma w\Delta^2/(N_{obs} - N_{par})]^{1/2}$.

Pyridyl-ylid complexes

The reaction was carried out as described above starting from 0.3 mmol (A)Rh(L_2), L_2 = DPyPE, DPyPP or 2 Me_2PPy. The (A)Rh(L_2) was converted

Table 8

Positional and equivalent isotropic thermal parameters for $1 \cdot CH_2Cl_2$

Atom	x	y	z	U_{eq}
Rh	0.84361(3)	0.14467(2)	0.24790(1)	0.0231(1)
Cl(1)	0.5680(1)	0.33444(9)	0.25915(4)	0.0415(3)
P(1)	1.09471(9)	−0.03679(8)	0.25422(3)	0.0250(2)
P(2)	0.9376(1)	0.24031(8)	0.31330(3)	0.0264(2)
O(1)	0.8907(3)	0.2716(2)	0.17888(9)	0.0324(7)
O(2)	0.7472(3)	0.0651(2)	0.1869(1)	0.0327(7)
N(1)	0.9274(3)	−0.1230(3)	0.3302(1)	0.0285(8)
N(2)	0.8690(4)	0.1432(3)	0.4131(1)	0.0407(9)
C(1)	0.7867(4)	0.0176(3)	0.3057(2)	0.030(1)
C(2)	1.0809(4)	−0.1611(3)	0.3131(1)	0.0282(9)
C(3)	1.3092(4)	−0.2825(4)	0.3388(2)	0.038(1)
C(4)	1.1771(5)	−0.3705(4)	0.3804(2)	0.048(1)
C(5)	1.0180(5)	−0.3341(4)	0.3948(2)	0.048(1)
C(6)	0.8932(5)	−0.2068(4)	0.3698(2)	0.040(1)
C(7)	1.1933(4)	−0.1488(3)	0.1953(1)	0.030(9)
C(8)	1.1200(5)	−0.1050(5)	0.1427(2)	0.061(1)
C(9)	1.1909(6)	−0.1843(7)	0.0960(2)	0.089(2)
C(10)	1.3341(6)	−0.3107(6)	0.1027(2)	0.076(2)
C(11)	1.4087(6)	−0.3558(5)	0.1552(2)	0.071(2)
C(12)	1.4308(5)	−0.2744(4)	0.2017(2)	0.053(1)
C(13)	1.236894)	0.0221(4)	0.2827(2)	0.032(1)
C(14)	1.1508(4)	0.1133(4)	0.3324(2)	0.032(1)
C(15)	0.8419(4)	0.2705(3)	0.3835(1)	0.0314(9)
C(16)	0.7545(4)	0.4067(4)	0.4050(2)	0.042(1)
C(17)	0.6946(5)	0.4118(5)	0.4594(2)	0.054(1)
C(18)	0.7202(5)	0.2830(5)	0.4907(2)	0.053(1)
C(19)	0.8076(5)	0.1512(5)	0.4656(2)	0.048(1)
C(20)	0.9353(4)	0.4107(3)	0.2841(1)	0.033(1)
C(21)	0.7874(5)	0.5344(4)	0.2716(2)	0.045(1)
C(22)	0.7847(6)	0.6624(4)	0.2475(2)	0.054(1)
C(23)	0.9267(6)	0.6686(4)	0.2334(2)	0.054(1)
C(24)	1.0739(6)	0.5476(4)	0.2442(2)	0.052(1)
C(25)	1.0799(5)	0.4174(4)	0.2703(2)	0.042(1)
C(26)	0.8347(4)	0.2905(3)	0.1285(1)	0.032(1)
C(27)	0.7297(4)	0.2367(4)	0.1096(2)	0.038(1)
C(28)	0.6929(4)	0.1309(4)	0.1377(1)	0.033(1)
C(29)	0.8973(4)	0.3723(4)	0.0844(2)	0.040(1)
C(30)	0.7609(8)	0.4857(8)	0.0451(3)	0.103(3)
C(31)	1.0187(8)	0.2569(7)	0.0466(3)	0.085(2)
C(32)	0.986(1)	0.4422(9)	0.1140(2)	0.096(3)
C(33)	0.5852(5)	0.0755(5)	0.1082(2)	0.048(1)
C(34)	0.4922(7	0.1722(7)	0.0559(2)	0.074(2)
C(35)	0.4651(8)	0.0651(9)	0.1524(2)	0.087(3)
C(36)	0.6967(9)	−0.0812(6)	0.0917(3)	0.095(3)
Cl(2)	0.5104(1)	0.8070(1)	0.39648(4)	0.0476(3)
Cl(3)	0.4354(1)	0.2413(1)	0.39517(5)	0.0597(4)
Cl(4)	0.1634(2)	0.2673(2)	0.46751(6)	0.0812(5)
C(37)	0.3756(6)	0.1664(5)	0.4560(2)	0.061(2)

within a few hours into the ylid complex [(A)Rh(Cl)(CH_2L_2)]Cl; no intermediate (A)Rh(Cl)(CH_2Cl)(L_2) could be detected by ^{31}P NMR spectroscopy. Evaporation of the solvent and washing with THF gave a light-yellow solid. The DPyPE complex (A = dpm; **1**) was crystallized very slowly (during several weeks) from CH_2Cl_2/THF to give a few X-ray quality crystals. Metathesis with $NaBPh_4$ gave [(A)Rh(Cl)(CH_2DPyPE)]BPh_4, which crystallized as very fine needles (much too thin for X-ray diffraction).

X-ray structure determination

Crystals of X-ray diffraction quality were obtained by crystallization of **1** from CH_2Cl_2/THF. A single crystal of suitable dimensions, cleaved from a larger rod, was mounted in a thin-walled glass capillary under nitrogen and held in place by an epoxy glue. All measurements were made on a Nicolet R3m diffractometer at room temperature, using graphite monochromated Mo-K_α X-radiation ($\lambda = 0.71069$ Å). Three check reflections remeasured after every 50 ordinary data showed 2% decay over the period of data collection; an appropriate correction was therefore applied, as were Lorentz and polarization corrections. The absorption correction was made numerically: Crystal faces [distances from origin in mm]: (−1 −1 1) [0.4], (1 1 −1)

Table 9

Selected bond lengths (Å) and angles (°) for **1**·CH_2Cl_2

(a) *Bond distances*					
Rh–Cl(1)	2.415(1)	Rh–P(1)	2.206(1)	Rh–P(2)	2.261(1)
Rh–O(2)	2.093(3)	Rh–C(1)	2.023(3)	P(1)–C(2)	1.840(3)
P(1)–C(13)	1.823(4)	P(2)–C(14)	1.831(4)	P(2)–C(15)	1.826(3)
O(1)–C(26)	1.262(4)	O(2)–C(28)	1.274(4)	N(1)–C(1)	1.510(4)
N(1)–C(6)	1.339(5)	N(2)–C(15)	1.345(4)	N(2)–C(19)	1.332(5)
C(3)–C(4)	1.389(5)	C(4)–C(5)	1.374(7)	C(5)–C(6)	1.379(6)
C(13)–C(14)	1.521(5)	C(15)–C(16)	1.386(5)	C(16)–C(17)	1.371(5)
C(17)–C(18)	1.378(6)	C(18)–C(19)	1.390(6)	C(26)–C(27)	1.402(5)
C(26)–C(29)	1.537(5)	C(28)–C(33)	1.541(6)	C(27)–C(28)	1.387(5)
Rh–O(1)	2.149(2)	P(2)–C(20)	1.812(3)	C(2)–C(3)	1.370(5)
P(1)–C(7)	1.815(3)	N(1)–C(2)	1.341(5)		
(b) *Bond angles*					
Cl(1)–Rh–P(1)	169.83(4)	Cl(1)–Rh–P(2)	90.60(4)		
Cl(1)–Rh–O(2)	86.99(7)	Cl(1)–Rh–C(1)	86.6(1)		
P(1)–Rh–O(1)	95.87(7)	P(1)–Rh–O(2)	98.87(7)		
P(2)–Rh–O(1)	91.30(7)	P(2)–Rh–O(2)	177.45(8)		
O(1)–Rh–O(2)	87.99(9)	O(1)–Rh–C(1)	173.1(1)		
Rh–P(1)–C(2)	102.8(1)	Rh–P(2)–C(14)	109.9(1)		
Rh–O(1)–C(26)	124.2(2)	Rh–O(2)–C(28)	123.9(2)		
C(1)–N(1)–C(6)	117.6(3)	C(2)–N(1)–C(6)	121.6(3)		
Rh–C(1)–N(1)	116.6(2)	P(1)–C(2)–N(1)	113.5(2)		
N(1)–C(2)–C(3)	120.4(3)	C(2)–C(3)–C(4)	118.9(4)		
C(4)–C(5)–C(6)	119.5(4)	N(1)–C(6)–C(5)	119.9(4)		
P(2)–C(14)–C(13)	110.8(3)	O(2)–C(28)–C(27)	125.9(4)		
O(1)–C(26)–C(27)	125.6(3)	P(1)–Rh–P(2)	83.63(4)		
C(26)–C(27)–C(28)	127.7(3)	Cl(1)–Rh–O(1)	92.62(7)		
P(1)–Rh–C(1)	85.6(1)	P(1)–C(2)–C(3)	126.1(3)		
P(2)–Rh–C(1)	95.5(1)	C(3)–C(4)–C(5)	119.5(4)		
O(2)–Rh–C(1)	85.2(1)	P(1)–C(13)–C(14)	106.2(3)		
Rh–P(1)–C(13)	111.3(1)	C(1)–N(1)–C(2)	120.8(3)		
C(2)–P(1)–C(13)	103.2(2)				

[0.4], (0 1 0) [0.25], (0 −1 0) [0.25], (0 0 1) [0.25], (0 0 −1) [0.25]. The structure was solved by conventional heavy-atom (Patterson and Fourier) methods. All non-hydrogen atoms were assigned anisotropic thermal parameters and refined without positional constraints. All hydrogens were constrained to idealized geometries (C–H = 0.96 Å; H–C–H = 109.5° for aliphatic hydrogens) and assigned fixed isotropic displacement parameters ca. 1.2 times U_{iso} of their attached carbon atom. The structure was refined by full-matrix blocked-cascade least-squares. All calculations were carried out on a Nicolet R3m/V structure determination system using programs of the SHELXTL-PLUS package [19]. Neutral-atom scattering factors were taken from Ref. 20. Details of the data collection and structure determination are gathered in Table 7; positional and equivalent isotropic thermal parameters are given in Table 8 and selected bond distances and angles in Table 9.

References and notes

1 P.H.M. Budzelaar, J.H.G. Frijns and A.G. Orpen, Organometallics, 9 (1990) 1222.

2 The chemical differences between the acac- and dpm-rhodium complexes are small; the dpm complexes are generally much more soluble in apolar solvents.

3 It is important not to use an excess of diphosphine to avoid side reactions. Even if the reactants are combined in a 1:1 ratio, complexes of the overall stoichiometry (A)Rh$(L_2)_2$ are initially formed in certain cases, but refluxing for 30 min in THF or benzene is sufficient to effect comproportionation of (A)Rh(COD) and (A)Rh$(L_2)_2$ to (A)Rh(L_2). The nature of the (A)Rh$(L_2)_2$ intermediates will be discussed in a separate paper (P.H.M. Budzelaar and A.G. Orpen, Organometallics, to be published), in which we will also describe some special reactions of the DPPM complexes.

4 A.J. Mukhedkar, V.A. Mukhedkar, M. Green, and F.G.A. Stone, J. Chem. Soc. A, (1970) 3166; D.M. Barlex, M.J. Hacker and R.D.W. Kemmitt, J. Organomet. Chem. 43 (1972) 425.

5 We also briefly investigated reactions of bis(monophosphine) complexes (A)RhL_2 with dichloromethane, mainly by ^{31}P NMR spectroscopy; the following summarizes the results. (A)Rh$(PPh_3)_2$ adds CH_2Cl_2 to give (A)Rh(Cl)$(CH_2Cl)(PPh_3)_2$ with *trans* phosphines. This complex reacts with pyridine to give (A)Rh(Cl)$(CH_2Cl)(PPh_3)$(Py) (two isomers) but does not form an ylid complex. Pyridylphosphines $Py_nPh_{3-n}P$ ($n = 1–3$) form complexes (A)RhL_2, which react with CH_2Cl_2 to give the ylid complexes [(A)Rh(Cl)(CH_2L)(L)]$^+$ Cl^-. These ylid complexes are obtained as mixtures of two or three (depending on n) slowly interconverting isomers with rather similar δ_P and ^1J(RhP) values. Thus, the reaction types described in the present paper are not restricted to diphosphines. However, the diphosphines have the advantage that they give products which are conformationally more stable and are more easily characterized.

6 P.E. Garrou, Inorg. Chem., 14 (1975) 1435; idem, Chem. Rev., 81 (1971) 229.

7 E. Breitmaier and W. Voelter, Carbon-13 NMR spectroscopy, 3rd Ed., Verlag Chemie, Weinheim, F.R.G., 1987, p. 286.

8 H. Werner, W. Paul, R. Feser, R. Zolk and P. Thometzek, Chem. Ber., 118 (1985) 261.

9 F.R. Kreissl and E.O. Fischer, Chem. Ber., 107 (1974) 183.

10 W.-K. Wong, W. Tam and J.A. Gladysz, J. Am. Chem. Soc., 101 (1979) 5400; W. Tam, G.-Y. Lin, W.-K. Wong, W.A. Kiel, V.K. Wong and J.A. Gladysz, ibid., 104 (1982) 141.

11 M. Keeton, R. Mason and D.R. Russel, J. Organomet. Chem., 33 (1971) 259.

12 G.C.A. Bellinger, H.B. Friedrich and J.R. Moss, J. Organomet. Chem., 166 (1989) 175.

13 E.G. Burns, S.S.C. Chu, P. de Meester and M. Lattman, Organometallics, 5 (1986) 2383.

14 J.R. Moss and J.C. Spiers, J. Organomet. Chem., 182 (1979) C20; R. Feser and H. Werner, Angew. Chem., 92 (1980) 960.

15 R.A. Lalancette, W. Furey, J.N. Costanzo, P.R. Hemmes and F. Jordan, Acta Crystallogr. B, 34 (1978) 2950.

16 F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen and R. Taylor, J. Chem. Soc., Perkin Trans. II, (1987) S1.

17 D.M. Barlex, A.C. Jarvis, R.D.W. Kemmitt and B.Y. Kimura, J. Chem. Soc., Dalton Trans., (1972) 2549.

18 D.A. Slack, D.L. Egglestone and M.C. Baird, J. Organomet. Chem., 146 (1978) 71.

19 G.M. Sheldrick, SHELXTL-PLUS Rev. 2.2, Göttingen, F.R.G., 1987.

20 International Tables for X-ray Crystallography, Kynoch Press, Birmingham, 1974, Vol. IV.