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Review

Coordination complexes of aryl- and alkylphosphonium cyclopentadienylides (cyclopentadienylidene ylides), $C_5R_4PR'R''R'''$ (R = H, alkyl, aryl; R′, R″, R‴ = alkyl, aryl)

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Contents

Abstract

The coordination chemistry of phosphonium cyclopentadienylides $C_5R_4PRR'R''R'''$ (R = H, alkyl, aryl; R′, R″, R‴ = alkyl, aryl) is reviewed critically. In part, perhaps, because of difficulties in characterizing many of the coordination complexes obtained in the early days, research on this class of potentially very interesting ligands stagnated and virtually no publications dealing with their coordination chemistry have appeared in over two decades. As a result, the reactivities of most of these compounds remain largely unexplored and the effects of ligand substitution on metal complex structures and reactivities have been very little examined. Although significant contributions on this subject have been made, much interesting chemistry remains to be examined and discovered using this class of ligand. If the weight of modern spectroscopic techniques is brought to bear on the some of the structural questions that have appeared in the literature, new insights may be garnered. This review does not deal with analogous groups 15 and 16 ylides which have been reported, such as those of sulphur, arsenic and antimony. Although these ylides are related to the phosphorus ylides, it is beyond the scope of this review to discuss their coordination chemistry.

Keywords: Coordination complexes; Aryl- and alkylphosphonium cyclopentadienylides; Cyclopentadienylidene ylides; Transition metals

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1. Phosphonium cyclopentadienylidene ligand syntheses

Triphenylphosphonium cyclopentadienylide ($C_5H_4PPh_3$; Fig. 1, **I**) was first reported in 1956 by Ramirez and Levy [1], who also explored its organic chemistry [2–6]. They found *inter alia* that $C_5H_4PPh_3$, oft referred to as the "Ramirez ylide", is unusually inert, for instance being unreactive with ketones unlike typical ylides. They attributed this unusual stability to the charge delocalization implied by resonance structure **Ib**, consistent with the relatively high dipole moment of 7.0 D [3]. Further evidence for delocalization of the π electron density was found in the crystal structure, which showed that the P–C_5, or P–C(ylide), bond was of intermediate length between those expected for P–C single and double bonds. In addition, the C_5 ring CC bond lengths were found to be rather similar to those of benzene although they also alternated somewhat as implied by structure **Ia** [7]. In addition, the ^{13}C NMR spectrum exhibited an unusually high field chemical shift for the ylide carbon and a P–C(ylide) coupling constant typical of an aliphatic carbon–P bond [8].

The interesting features of this compound from an organometallic point of view becomes apparent when resonance structure **Ib** is examined. This resonance form is structurally akin to and isoelectronic with the anionic cyclopentadienyl (Cp) ligand, ubiquitous in organometallic chemistry and catalysis. Thus the phosphonium cyclopentadienylide class of ligands, with significantly different steric and electronic properties from those of Cp, should lend itself to the tuning of catalyst properties to give unique reactivities. In addition a number of potential modes of coordination exist (η^{1-5}), with two modes already demonstrated (η^5 and η^1) [9–32]. With these potential applications, it is surprising that this class of ligand has 'fallen by the wayside', virtually no publications dealing with the coordination chemistry of $C_5H_4PPh_3$ having appeared in over two decades.

One of the major limitations to the development and utilization of this class of compounds is the lack of general synthetic procedures; there exist only a few synthetic methods to produce phosphonium cyclopentadienylides, each with its own drawback. The lack of a general synthetic route has resulted in very few phosphonium cyclopentadienylides being known, and in very few metal complexes having been prepared beyond those of $C_5H_4PPh_3$. The following sections detail the different preparations for phosphonium cyclopentadienylides which have been reported, some of them unrecognized.

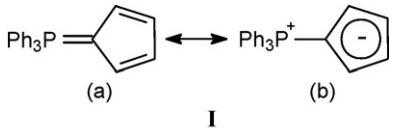

Fig. 1. The resonance forms of the Ramirez ylide ($C_5H_4PPh_3$).

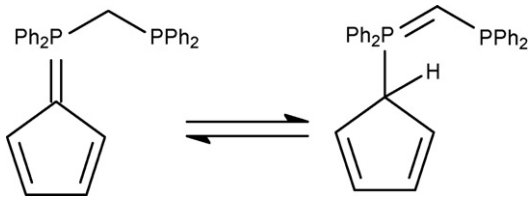

Fig. 3. The chelating (bis(diphenylphosphino)methane derived ylide and its tautomerization.

1.1. Synthesis of the Ramirez ylide ($C_5H_4PPh_3$)

The Ramirez ylide, $C_5H_4PPh_3$, was synthesized using the method shown in Fig. 2 [3]. The first step in this scheme reported by Ramirez et al. was the reaction of two equivalents of triphenylphosphine with dibromocyclopentene, which was prepared by the *in situ* reaction of cyclopentadiene and bromine. After reaction with triphenylphosphine, the diphosphonium salt was produced and then converted into the phosphonium cyclopentadienylide by reaction with two equivalents of NaOH. Two processes occurred during this step. First, one equivalent of phosphine was displaced during the deprotonation of the ring, although the product was not isolated during the reaction. Second, the C_5 ring was deprotonated by the second equivalent of NaOH to yield the ylide in 41% yield.

1.2. Synthesis of other ylides

Ramirez did not report attempts to extend his method to prepare other ylides [3], and some attempts to extend this method to other phosphines have produced only black, insoluble tars which were probably polymeric materials [33]. However, there does exist one report extending this method to a low yield synthesis of the tri-*n*-propyl derivative $C_5H_4P(n\text{-}Pr)_3$ [34] and the Ramirez methodology was also used to synthesize the chelating bis(diphenylphosphino)methane derivatives shown in Fig. 3

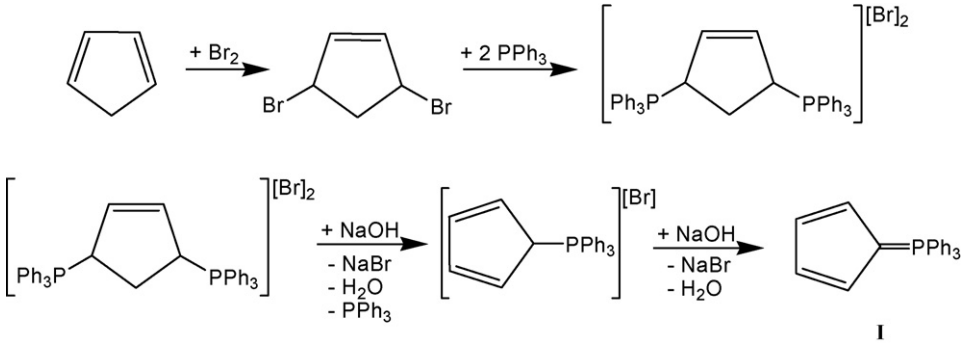

Fig. 2. The synthesis of $C_5H_4PPh_3$.

[35]. As in the first step of the Ramirez synthesis, dibromocyclopentadiene was prepared *in situ* before being added to the phosphine. After deprotonation, however, the resulting ylide was collected in poor yield (14%) because it was unstable and underwent polymerization. Thus, although the Ramirez procedure provides $C_5H_4PPh_3$ in reasonable yield, it does not seem to offer a general route to other phosphonium cyclopentadienylides.

In an alternative procedure, the ylide $C_5H_4PMePPh_2$ was prepared by Mathey and Lampin in 1975 via the method shown in Eqs. (1)–(3) [36]. The procedure was later developed further by Brownie et al. [37,38].

$$PClPh_2 + TlCp \rightarrow PCpPh_2 \quad (1)$$

$$PCpPh_2 + MeI \rightarrow [PMeCpPh_2]I \quad (2)$$

$$[PMeCpPh_2]I + BuLi \rightarrow C_5H_4PMePh_2 \quad (3)$$

Mathey et al. explored aspects of the chemistry of this ylide, but did not investigate its coordination chemistry. The Mathey synthetic method begins with the synthesis of cyclopentadienyldiphenylphosphine from chlorodiphenylphosphine followed by reaction *in situ* with methyl iodide to provide the phosphonium iodide as shown in Eq. (2). The final step involved deprotonation of the phosphonium iodide by *n*-butyllithium (Eq. (3)). Mathey reported the yield of the final step to be 70%.

Very recently there has been reported a re-examination of the synthesis, structure, bonding and chemistry of the Mathey ligand, methyldiphenylphosphonium cyclopentadienylide ($C_5H_4PMePh_2$) [37]. The crystal structure of $C_5H_4PMePh_2$ has been determined and compared with that of $C_5H_4PPh_3$, discussed above, and the electronic structure of $C_5H_4PMePh_2$ has also been investigated using DFT methodologies [37]. The latter show that the almost degenerate HOMO and (HOMO-1) orbitals (Fig. 4a and b) are of symmetries rather similar to those of the corresponding HOMO (doubly degenerate; E_1 symmetry) of the cyclopentadienyl anion, and that a lower energy, relatively symmetric orbital (Fig. 4c) corresponds to the fully symmetric (A_1) bonding MO of the cyclopentadienyl anion. These results are consistent with the electronic structure implied by resonance for (b) of Fig. 5, and there appears not to be significant π involvement of a ring orbital with an orbital on the phosphorus atom, also consistent with the low P–C bond order implicit in zwitterionic structure (b) of Fig. 5 [37].

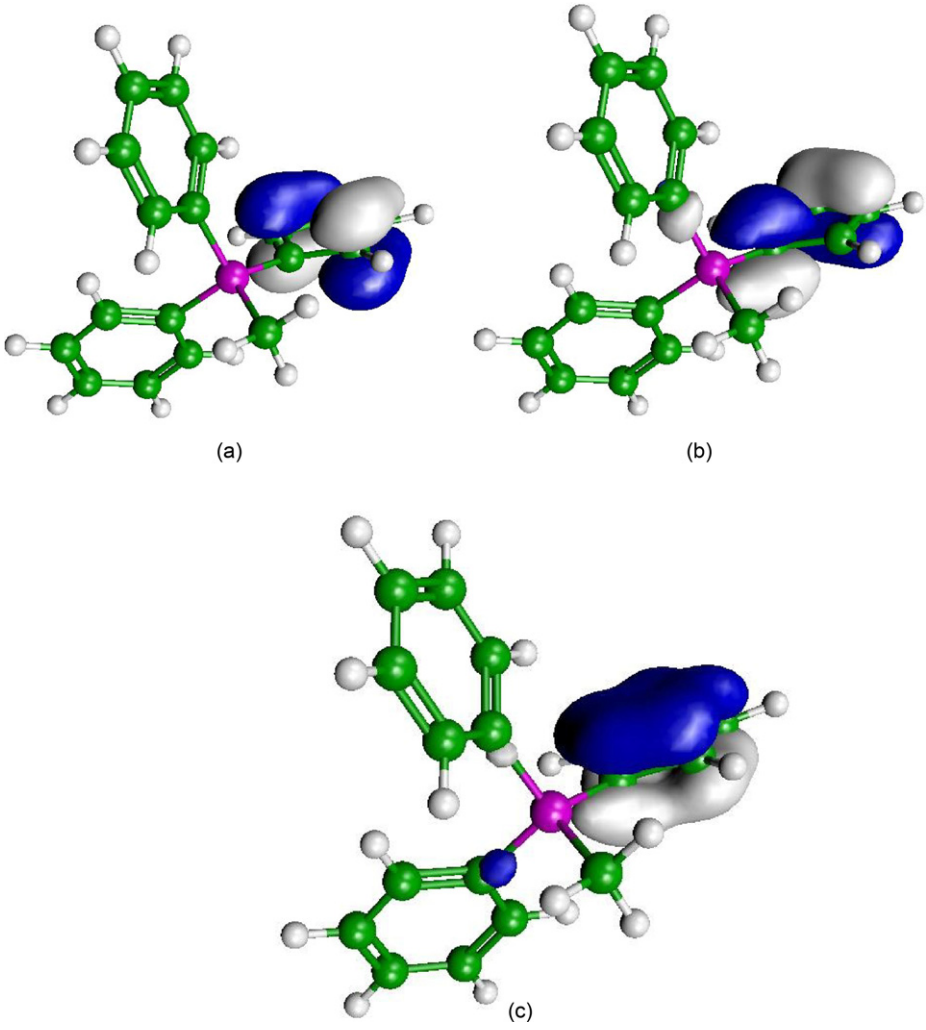

Fig. 4. Contour plots of the HOMO (a), (HOMO-1) (b) and (HOMO-6) (c) of $C_5H_4PMePh_2$.

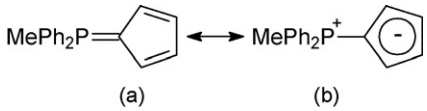

Fig. 5. Resonance structures of $C_5H_4PMePh_2$.

The Mathey synthetic route requires the use of a chlorodisubstituted phosphine, of which few are readily available. In addition, compounds of the type $CpPR_2$ are generally unstable at room temperature, presumably because of Diels–Alder dimerization, and must be converted into phosphonium salts immediately [39]. These two limitations prevent this method from providing a general route into phosphonium cyclopentadienylides. However, chemistry as in Eq. (2) can lead in principle to new phosphonium cyclopentadienylides because alkyl halides other than methyl iodide can be used. Unfortunately this approach does not seem to have been assessed.

Prior to Mathey et al.'s report on the synthesis of $C_5H_4PMePPh_2$, Freeman et al. published the preparation of the tetraphenylcyclopentadienylidene derivative of $C_5H_4PPh_3$, shown in Fig. 6 [40]. In this synthesis, PPh_3 is added to 5-bromo-1,2,3,4-tetraphenylcyclopentadiene to yield the phosphonium bromide. The anion was then exchanged for perchlorate, ClO_4^-, and the resulting perchlorate salt was deprotonated with NaOH to give the ylide in excellent yield. The presence of the bulky substituents on the bromocyclopentadiene moiety gives this molecule much greater stability than is the case with, e.g. bromocyclopentadiene. Triphenylphosphonium 2,3,4-triphenylcyclopentadienylide was also synthesized by the same group using this methodology [41].

1.3. Synthesis of phenyl substituted phosphonium cyclopentadienylides via diazocyclopentadienes

An alternative procedure involves the use of diazocyclopentadienes to generate phosphonium cyclopentadienylides via reactions with phosphines. Ramirez initially tried to use this method to generate $C_5H_4PPh_3$, shortly after his initial report of the synthesis discussed above [42]. Diazocyclopentadiene was reacted with triphenylphosphine to yield the phosphazine shown in Fig. 7, but all attempts to thermally decompose the phosphazine failed and Ramirez abandoned this method as a route into phosphonium cyclopentadienylides [42].

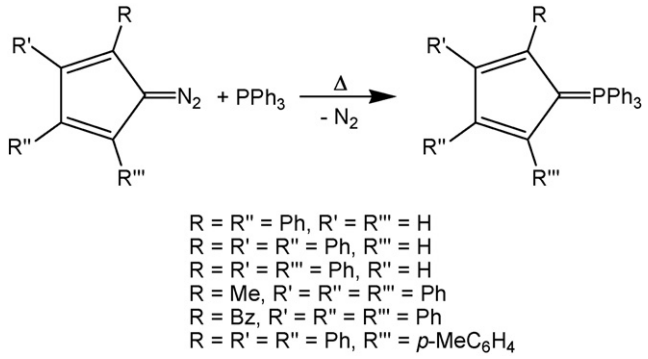

Fig. 8. The synthesis of ylides from substituted diazocyclopentadienes.

Freeman and co-workers revived this methodology and succeeded in generating a number of substituted cyclopentadienyl derivatives of $C_5H_4PPh_3$ [43,44]. The reactions were performed by grinding the diazo-compounds and triphenylphosphine together and then heating (150–160 °C) the resulting mixtures under an inert atmosphere until the evolution of gas ceased (10–60 min) (Fig. 8) [43]. Yields were 26–68% depending upon the diazo-compound used [43]. This method is useful in preparing some C_5 ring substituted derivatives of $C_5H_4PPh_3$, but the failure of Ramirez et al. demonstrates that this is not a general route into these ylides.

1.4. Synthesis of $C_9H_6PPh_3$, the indenyl analogue

In 1967, Crofts and Williamson reported the preparation of $C_9H_6PPh_3$, the indenyl analogue of $C_5H_4PPh_3$ [45]. In this synthesis, indenyl bromide was reacted with PPh_3 to give the phosphonium salt $[C_9H_6PPh_3]Br$, which was subsequently deprotonated to furnish the ylide $C_9H_6PPh_3$ in modest yield. This method was not extended to other phosphines and, before a recent report in 2004 [46], $C_9H_6PPh_3$ was the only known indenyl derived phosphonium ylide.

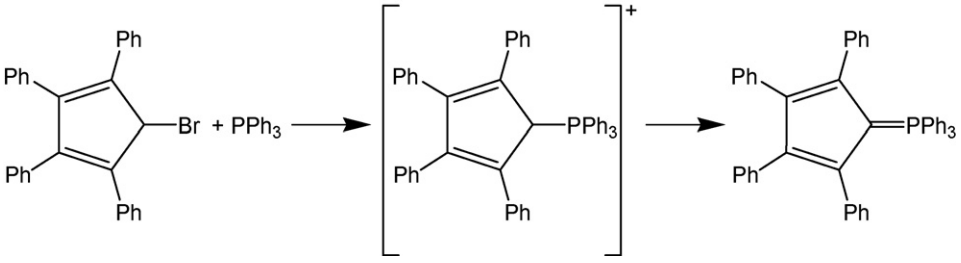

Fig. 6. The synthesis of $(C_5Ph_4)PPh_3$.

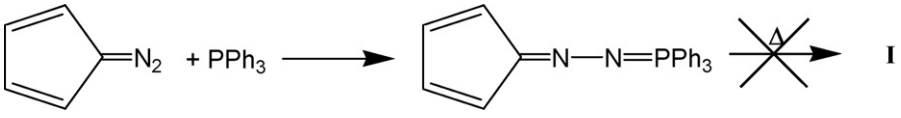

Fig. 7. The attempted synthesis of $C_5H_4PPh_3$ using diazocyclopentadiene.

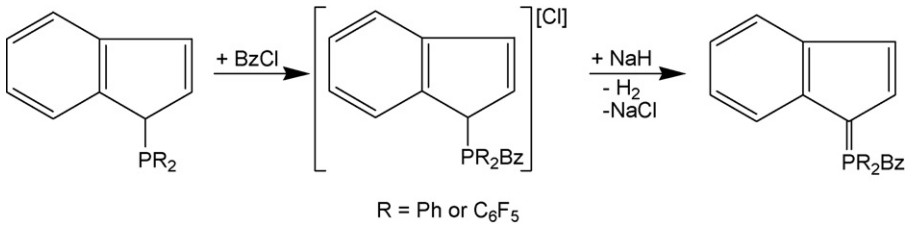

Fig. 9. The synthesis of indenyl derived phosphorus ylides.

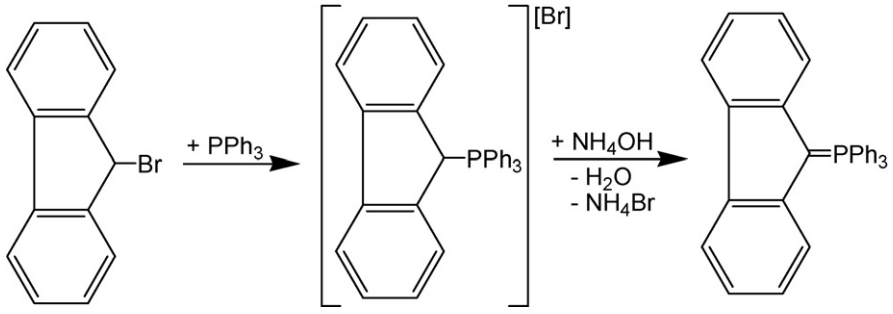

Fig. 10. The synthesis of the fluorenyl derived triphenylphosphine ylide.

The methodology developed by Mathey was extended to indenyl derivatives of phosphonium cyclopentadienylides in a 2004 report by Rufanov et al. [46] although the authors seem to have been unaware of Mathey's earlier report [36]. In this work, benzyl chloride was added to $IndPR_2$ (R = Ph, C_6F_5) to provide the corresponding phosphonium salts, $[IndPR_2CH_2Ph]Cl$, which were deprotonated by NaH to give the ylides, $C_9H_6PR_2CH_2Ph$ (Fig. 9). The use of indenyl in place of Cp has the advantage that $IndPR_2$ is stable and can be stored without the decomposition observed with $CpPR_2$ derivatives.

1.5. Synthesis of fluorenyl analogues of phosphonium ylides

In addition to the indenyl derivatives, many fluorenyl derivatives are also known for this class of compound. The first successful synthesis of triphenylphosphonium fluorenylide was reported in 1947 by Pinck and Hilbert [47] who found that reaction of 9-bromofluorene with triphenylphosphine gave the corresponding phosphonium salt in nearly quantitative yield. The fluorenyl phosphonium salt was then deprotonated with aqueous ammonia to give the ylide as in Fig. 10 [47].

Because of the ready availability of 9-bromofluorene, many derivatives of triphenylphosphoniumfluorenylide have been synthesized using this same methodology [47] and a variety of fluorenyl phosphonium ylides, with substitution of the phosphorus R groups, have been reported. In addition, 9-bromofluorene derivatives with substituents on the aryl rings have been used to give even more variety for this class of ligand [48]. The use of bromo-derived 'Cp'-like precursors has thus been demonstrated as an excellent route into the direct precursors for various types of phosphonium cyclopentadienylides and should be a potentially useful route to such ligands.

In addition to these ylides, Holy et al. [35] and Schmidbaur and Deschler [49] have reported the syntheses of several chelating phophonium fluorenylidene ylides, as shown in Fig. 11. The addition of 9-bromofluorene to the diphosphines gave the monophosphonium bromide salts which were then deprotonated. When the ethylene and propylene bridged diphosphines were used, diphosphonium salt formation was also observed. In the case of the ethylene derivative, the formation of the diphosphonium salt could be minimized (<20%) by short reaction times and the addition of an excess of the diphosphine. Deprotonation of the ethylene bridged diphosphonium salt did not afford

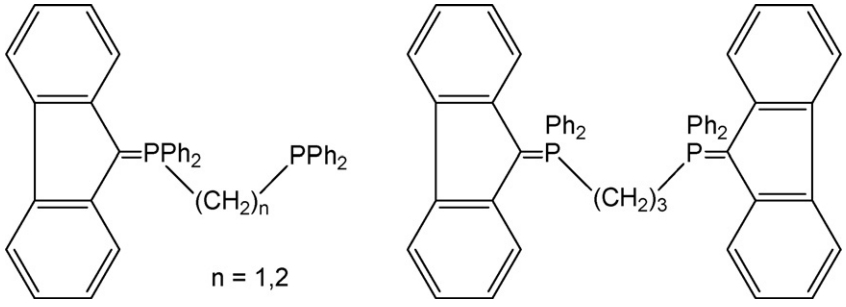

Fig. 11. Chelating fluorenyl derived ylides and the fluorenyl bis-ylide.

the bis-ylide, but rather a highly insoluble, unidentified solid. Deprotonation of the ethylene bridge to form a vinylphosphorane which could then polymerize was presumed to be occurring [35].

For the propylene derivative, reaction mixtures always contained the diphosphonium salt as the major product under all reaction conditions, preventing the isolation of the pure monophosphonium salt and mono-ylide. In contrast to the methylene and ethylene bridged diphosphines, the propylene bridged bis-ylide was easily generated in good yield (85%) from the diphosphonium salt by deprotonation with Na_2CO_3 [35].

2. Metal complexes of phosphonium cyclopentadienylides

In view of the significance of resonance structures of the type **Ib** and the similarity to the aromatic cyclopentadienyl ligand, a number of metal complexes of phosphonium cyclopentadienylides and analogues have been reported. This section will describe research done on the coordination chemistry of the respective transition metal and main group metal families. Following the discussion, Tables 1 and 2 present overviews of the available NMR and structural (crystallographic) data, respectively.

2.1. Group 4 metals

Very little work has been reported on the synthesis of compounds of the group 4 metals. The first such report, by Holy et al. [30], appeared in 1977 and describes the reaction of $C_5H_4PPh_3$ with the group 4 metal halides as in the following equation:

$$nC_5H_4PPh_3 + MCl_x \rightarrow (C_5H_4PPh_3)_nMCl_x$$
$$(M = Ti, Zr, Hf;\ n = 1, 2;\ x = 3, 4) \quad (4)$$

Titanium tetrachloride gave a tan precipitate which was characterized by IR and ^{1}H NMR spectroscopy and elemental analyses and identified as $[(\eta^5\text{-}C_5H_4PPh_3)_2TiCl_2]Cl_2$ although no crystals suitable for X-ray analysis were obtained. The ^{1}H NMR spectrum exhibited resonances at δ 6.30–6.65 for the C_5H_4 ring protons [30]. When $TiCl_3$ was stirred with one equivalent of $C_5H_4PPh_3$, a product identified as $(C_5H_4PPh_3)TiCl_3{\cdot}4H_2O$ was obtained, but all attempts to prepare a Ti(II) compound failed [30].

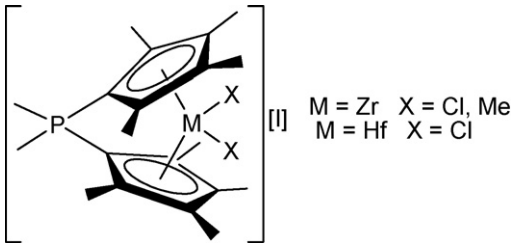

Fig. 12. The ansa-zirconocene- and ansa-hafnocene-like complexes of the phosphonium bridged permethylcyclopentadienyl ligand.

Zirconium tetrachloride was found to react with $C_5H_4PPh_3$ to produce a substance thought to be the mono-ylide compound $[C_5H_4PPh_3ZrCl_3]Cl$ although it was too insoluble to recrystallize and the reported elemental analyses did not in fact agree well with the composition suggested. Hafnium tetrachloride also reacted with $C_5H_4PPh_3$, giving an apparent 1:1 product that could not be identified [30].

More recently, in 2000, Shin et al. reported the syntheses of ansa-zirconocene and -hafnocene compounds of phosphonium bridged permethylcyclopentadienyl ligands [50], shown in Fig. 12; the dichlorozirconocene and hafnocene analogues were characterized by X-ray crystallography. This paper does not consider the ligand to be a phosphonium cyclopentadienylide, but the resonance structures shown in Fig. 13 exhibit a pronounced similarity to those of $C_5H_4PPh_3$ (Fig. 1). The P–C_5Me_4 bonds are equivalent and are 1.800(2) Å for the zirconium compound, 1.792(2) Å for the hafnium compound [50], considerably longer than are observed in other complexes of Ramirez-type ylides (Table 2) and indicating that the P–C bonds are intermediate between single and a double bonds but closer to the former. The dichlorozirconocene compound was converted to the dimethyl analogue by reaction with MeMgI (Fig. 14). The dimethyl compound was in turn reacted with CO, which inserted into one of the metal–alkyl bonds to provide the aryl C(O)–Me compound [50].

2.2. Group 6 metals

Phosphonium cyclopentadienylide complexes of the group 6 metals are the most thoroughly investigated group of complexes of the Ramirez-type ligands. Wilkinson noted soon after the initial Ramirez report that, since an electronic struc-

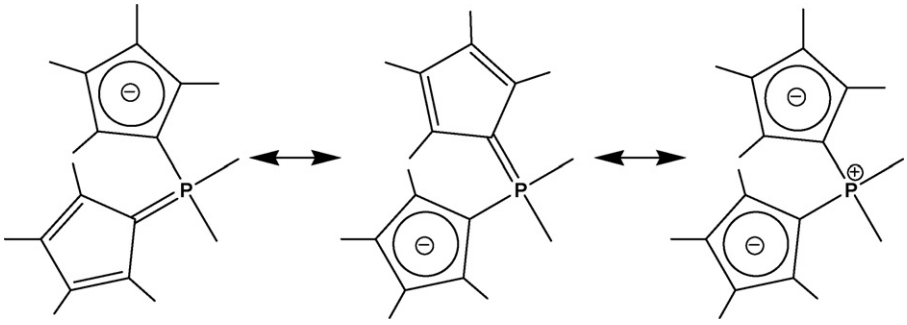

Fig. 13. The structure of the phosphonium bridged permethylcyclopentadienyl ligand.

Table 1
Representative NMR data

Compound	Solvent	δ (C_5H_4)	δ (^{31}P)	Reference
$C_5H_4PPh_3$	$CDCl_3$	6.47	–	[17]
$C_5H_4PMePh_2$	CD_2Cl_2	6.29, 6.44	7.95	[37]
Group 4				
"[(η^5-$C_5H_4PPh_3$)$_2$$TiCl_2$][Cl]$_2$"	DMSO-d_6	6.30–6.65 (m)	–	[30]
Group 6				
(η^5-$C_5H_4PPh_3$)$Cr(CO)_3$	$CHCl_3$	4.65 (m), 4.92 (m)	–	[10]
(η^5-$C_5H_4PPh_3$)$Mo(CO)_3$	$CHCl_3$	5.23 (m), 5.49 (m)	–	[10]
(η^5-$C_5H_4PPh_3$)$W(CO)_3$	$CHCl_3$	5.22 (m), 5.49 (m)	–	[10]
(η^5-$C_5H_4PMePh_2$)$Cr(CO)_3$	CD_2Cl_2	4.71, 4.90	19.54	[37]
(η^5-$C_5H_4PMePh_2$)$Mo(CO)_3$	CD_2Cl_2	5.29, 5.48	18.25	[37]
(η^5-$C_5H_4PMePh_2$)$W(CO)_3$	CD_2Cl_2	5.21, 5.46	18.58	[37]
[(η^5-$C_5H_4PMePh_2$)$Mo(CO)_3$I]I	CD_2Cl_2	6.04, 6.43	21.08	[37]
[(η^5-$C_5H_4PPh_3$)$Cr(CO)_3$H]$^+$	CF_3COOH	5.20 (m), 5.42 (m)	–	[10]
[(η^5-$C_5H_4PPh_3$)$Mo(CO)_3$H]$^+$	CF_3COOH	5.69 (m), 5.91 (m)	–	[10]
[(η^5-$C_5H_4PPh_3$)$W(CO)_3$H]$^+$	CF_3COOH	5.73 (m), 6.00 (m)	–	[10]
"[($C_5H_4PPh_3$)$_2$$WCl_2$][Cl]$_4$"	CD_3CN	8.57 (m)	–	[31]
"($C_5H_4PPh_3$)$MCl_3(OH)_2$"	CD_3NO_2	7.7 (br m)	–	[31]
Group 7				
[(η^5-$C_5H_4PPh_3$)$Mn(CO)_3$][PF_6]	Acetone-d_6	5.83	–	[16]
[(η^5-$C_5H_4PPh_3$)$Re(CO)_3$][PF_6]	Acetone-d_6	6.27	–	[17]
Group 8				
[(4-X-$C_6H_4CH_2PPh_2$(η^5-C_5H_4))Fe(η^5-C_5H_5)][BF_4]				
X = H	$CDCl_3$	4.02 (m), 4.59 (m)	27.60	[56]
X = OMe	$CDCl_3$	4.25 (m), 4.73 (m)	26.25	[56]
X = F	$CDCl_3$	4.31 (t), 4.86 (t)	27.97	[56]
X = CN	$CDCl_3$	4.33 (t), 4.87 (t)	28.78	[56]
[(η^5-$C_5H_4PPh_3$)$Ru_6C(CO)_{14}$]	Acetone-d_6	4.92 (m), 5.16 (m)	21.46	[20]
[(η^5-$C_5H_4PMe_3$)Ru(C_5H_4OH)][PF_6]	Acetone-d_6	5.00 (m), 5.06 (m)	–	[57]
[(η^5-$C_5H_4PCy_3$)Ru(C_5H_4OH)][PF_6]	CD_3CN	4.85 (m), 4.92(m)	–	[57]
[(η^5-$C_5H_4PPh_3$)Ru(C_5H_4OH)][PF_6]	CD_3CN	4.83 (m), 5.09 (m)	–	[57]
[(η^5-$C_5H_4PPh_3$)Ru($C_5H_4OCOC_2H_5$)][PF_6]	Acetone-d_6	5.12 (m), 5.29 (m)	–	[57]
[(η^5-$C_5H_4PPh_3$)Ru(η^4-C_5H_4O)Br][PF_6]	CD_3NO_2	6.25 (m), 6.32 (m)	–	[57]
[(η^5-C_5H_5)RuFvRu(η^5-$C_5H_4PPh_3$)][BF_4]	CD_3NO_2	Peaks not assigned	25.08	[58]
Group 9				
[(η^5-$C_5H_4PEt_3$)$CoH(PEt_3)_2$][BF_4]$_2$	Acetone-d_6	5.6 (m), 6.3 (m)	–	[60]
[(η^5-$C_5H_4PPh_3$)$Rh(CO)_2$][PF_6]	$CDCl_3$	5.57 (m), 6.04 (m)	–	[21]
[(η^5-$C_5H_4PPh_3$)Rh(1,5-COD)][PF_6]	$CDCl_3$	4.92 (m), 5.86 (m)	–	[21]
[(η^5-$C_5H_4PPh_3$)Rh(nbd)][PF_6]	$CDCl_3$	4.94 (m), 5.78 (m)	–	[21]
[(η^5-$C_5H_4PPh_3$)Rh(CO)PPh_3][PF_6]	$CDCl_3$	4.92(m), 5.77 (m)	–	[21]
[(η^5-$C_5H_4PPh_3$)Rh(CO)(dmme)Rh(η^5-$C_5H_4PPh_3$)(CO)][PF_6]$_2$	$CDCl_3$	4.88 (m), 5.74 (m)	–	[21]
[(η^5-$C_5H_4PPh_3$)Rh(CO)(dmmb)Rh(η^5-$C_5H_4PPh_3$)(CO)][PF_6]$_2$	$CDCl_3$	4.90 (m), 5.78 (m)	–	[21]
[(η^5-$C_5H_4PPh_3$)Rh(C_5Me_5)][PF_6]$_2$	DMSO-d_6	6.25 (m)	–	[21]
Group 10				
[(η^3-($Ph_3PCHCHCH_2$)Pd(η^5-$C_5H_4PPh_3$)][BF_4]$_2$	$CDCl_3$	5.60 (m), 5.75 (m), 6.05 (m)	–	[25]
[(η^3-Allyl)Pd(η^5-$C_5H_4PPh_3$)][BF_4]$_2$	$CDCl_3$	6.33 (m)	–	[25]
[(η^5-$C_5H_4PPh_3$)Pd(1,5-COD)][BF_4]$_2$	Acetone-d_6	6.92 (m), 7.18 (m)	–	[26]
[(η^5-$C_5H_4PPh_3$)Pd(nbd)][BF_4]$_2$	Acetone-d_6	6.75–7.05 (m)	–	[26]
(η^5-$C_5H_4PPh_3$)Pd($C_4(CO_2Me)_4$)	$CDCl_3$	5.58 (m), 6.15 (m)	–	[24]
[(η^5-$C_5H_4PPh_3$)Pt(1,5-COD)][PF_6]$_2$	Acetone-d_6	6.90 (m)	–	[22]
[(η^5-$C_5H_4PPh_3$)Pt(nbd)][PF_6]$_2$	Acetone-d_6	6.88 (m)	–	[22]
[(η^5-$C_5H_4PPh_3$)Pt(COT)][PF_6]$_2$	Acetone-d_6	6.96 (m), 7.10 (m)	–	[22]
Group 12				
[(η^1-$C_5H_4PPh_3$)HgI_2]$_2$	$CDCl_3$	6.0–6.6 (m)	–	[28]

ture of type **Ib** would be isoelectronic with benzene, the ylide might be expected to form compounds of the type (η^5-$C_5H_4PPh_3$)$M(CO)_3$ (M = Cr, Mo, W), analogous to the known arene compounds (η^6-C_6H_6)$M(CO)_3$ [9]. Successful attempts to prepare the group 6 compounds were carried out and the molybdenum compound was obtained analytically pure [9]. The compounds were characterized by ^{1}H NMR and IR spectroscopy and η^5-structures were suggested although the structures and

Table 2
Representative bond length data (Å)

Compound	P–C_5	C(1)–C(2), C(1)–C(5)	C(2)–C(3), C(4)–C(5)	C(3)–C(4)	Reference
$C_5H_4PPh_3$	1.718(2)	1.430(3), 1.419(3)	1.392(4), 1.376(4)	1.401(4)	[7]
$C_5H_4PMePh_2$					
Molecule 1	1.7277(17)	1.429(3), 1.414(3),	1.374(3). 1.384(3),	1.405(3),	[37]
Molecule 2	1.7268(17)	1.413(2), 1.429(2)	1.384(2), 1.383(3)	1.407(3)	
Group 6					
(η^5-$C_5H_4PPh_3$)$Cr(CO)_3$					
Molecule 1	1.751(5)	1.431(8), 1.430(8)	1.452(9), 1.422(9)	1.394(10)	[15]
Molecule 2	1.755(6)	1.443(9), 1.441(8)	1.403(8), 1.386(9)	1.443(9)	[15]
(η^5-$C_5H_4PMePh_2$)$Cr(CO)_3$	1.759(3)	1.427(4), 1.429(4)	1.392(4), 1.397(4)	1.422(4)	[37]
(η^5-$C_5H_4PMePh_2$)$Mo(CO)_3$	1.759(3)	1.434(3), 1.430(3)	1.403(3), 1.400(3)	1.417(3)	[37]
(η^5-$C_5H_4PMePh_2$)$W(CO)_3$	1.765(4)	1.435(6), 1.438(6)	1.405(7), 1.393(7)	1.402(7)	[37]
[(η^5-$C_5H_4PMePh_2$)$Mo(CO)_3$I]I					
Molecule 1	1.780(8)	1.436(10), 1.440(10)	1.428(11), 1.385(11)	1.401(11)	[37]
Molecule 2	1.775(9)	1.437(11), 1.412(11)	1.418(12), 1.415(11)	1.386(12)	[37]
Group 8					
[($C_6H_5CH_2PPh_2$(η^5-C_5H_4))Fe(η^5-C_5H_5)][Cl]	1.768(3)	1.453(4), 1.432(4)	1.418(5), 1.425(5)	1.406(5)	[55]
[(4-OMe–$C_6H_4CH_2PPh_2$(η^5-C_5H_4))Fe(η^5-C_5H_5)][BF_4]	1.780(3)	–	–	–	[56]
[(η^5-$C_5H_4PPh_3$)$Ru_6C(CO)_{14}$]	1.793(12)	1.39(2), 1.43(2)	1.42(2), 1.41(2)	1.40(2)	[20]
[(η^5-$C_5H_4PCy_3$)Ru(η^5-C_5H_4OH)][PF_6]	1.790(3)	1.428(5), 1.443(5)	1.416(5), 1.416 (5)	1.403(6)	[57]
[(η^5-C_5H_5)RuFvRu(η^5-$C_5H_4PPh_3$)][BF_4]	1.769(3)	1.432(4), 1.439(4)	1.411(5), 1.430(5)	1.402(5)	[58]
Group 9					
[(η^5-$C_5H_4PPh_3$)$Co(CO)_2$][$Co(CO)_4$]	1.765(6)	1.426(9), 1.414(9)	1.395(10), 1.406(10)	1.375(12)	[18,19]
[(η^5-$C_5H_4PPh_3$)Rh(1,5-COD)][BPh_4]	1.76(1)	1.40(1), 1.41(1)	1.39(1), 1.37(1)	1.39(1)	[27]
Group 10					
(η^5-$C_5H_4PPh_3$)Pd($C_4(CO_2Me)_4$)	1.776(9)	1.40(1), 1.46(1)	1.47(1), 1.39(1)	1.42(2)	[24]

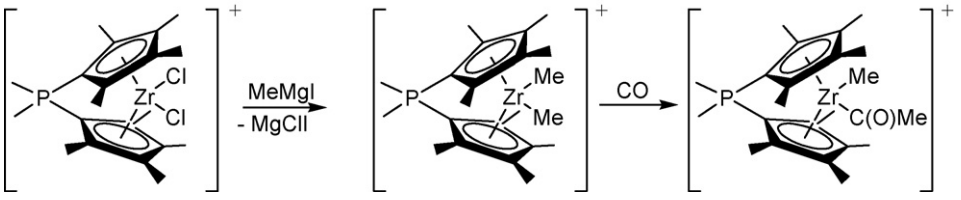

Fig. 14. Methylation and carbonylation reactions of the ansa-zirconocene compound shown in Fig. 12.

chemistry of these compounds were in fact only explored many years later [10–12].

Kotz and Pedrotty first reported the first detailed synthetic procedures for the group 6 tricarbonyl compounds [10], excesses of the metal hexacarbonyls, $Cr(CO)_6$ and $Mo(CO)_6$, being refluxed in diglyme with $C_5H_4PPh_3$ to provide the tricarbonyl compounds (η^5-$C_5Ph_4PPh_3$)$M(CO)_3$ (M = Cr, Mo) in good yields [10]. For tungsten, the tris-acetonitrile tricarbonyl precursor, $W(CO)_3(CH_3CN)_3$, was heated to 110 °C in diglyme with $C_5H_4PPh_3$ to generate the tungsten compound since little or no product was isolated when $W(CO)_6$ was used. The general reaction scheme is shown in Fig. 15. The new compounds were characterized by IR and ^{1}H NMR spectroscopy. The tetraphenylcyclopentadienylidene derivative of molybdenum (η^5-$C_5Ph_4PPh_3$)$Mo(CO)_3$, was also synthesized by heating an excess of $Mo(CO)_3(CH_3CN)_3$ with the phosphonium cyclopentadienylide, $C_5Ph_4PPh_3$, in refluxing THF [11]. This gave the desired product in 60% yield.

Kotz and Pedrotty also reacted the tricarbonyl compounds (η^5-$C_5H_4PPh_3$)$M(CO)_3$ (M = Cr, Mo, W) with trifluoroacetic

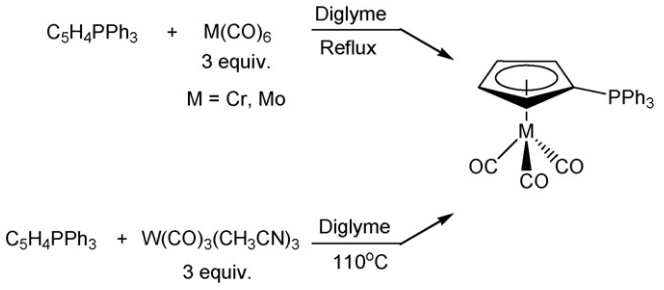

Fig. 15. The synthesis of the group 6 tricarbonyl complexes of $C_5H_4PPh_3$.

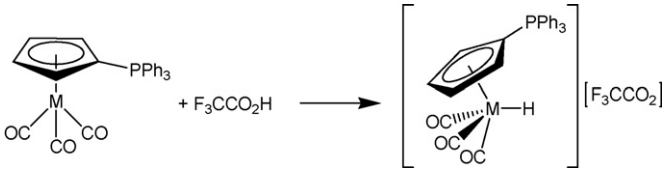

Fig. 16. The reaction of group 6 tricarbonyl complexes with F_3CCO_2H (M = Cr, Mo, W).

Fig. 17. The formation of the Lewis acid-base adducts of BF_3 and the group 6 tricarbonyl complexes of $C_5H_4PPh_3$.

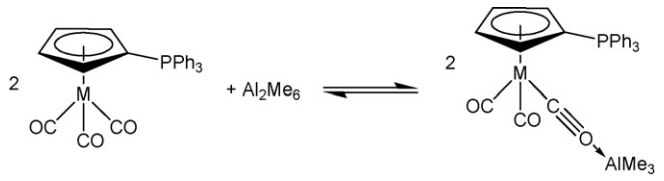

Fig. 18. The reaction of Al_2Me_6 with $(\eta^5\text{-}C_5H_4PPh_3)M(CO)_3$ to form the carbonyl oxygen bound Lewis acid-base adduct.

acid to generate the protonated cationic metal compounds (Fig. 16) [10] for which ^1H NMR spectroscopy revealed high field resonances (δ −5 to −8) characteristic of metal hydrides. Further evidence for the presence of a direct W–H bond was provided by the observation of ^{183}W–^1H spin–spin coupling. IR spectroscopy also showed the expected increase in CO stretching frequencies from those of the neutral precursors, but the ν(M–H) were not observed [10].

Reactions of the metal compounds $(\eta^5\text{-}C_5H_4PPh_3)M(CO)_3$ (M = Cr, Mo, W) with the Lewis acid BF_3 were also carried out (Fig. 17). It was determined that the coordination of BF_3 was reversible (tensimetric titrations) as no change in vapour pressure occurred when more than one equivalent of BF_3 had been added [10]. In addition, removal of the volatile materials from the reaction mixture always resulted in recovery of the starting materials (IR). IR spectra of these reactions exhibited new broad bands at ∼1050 cm^{-1}, consistent with the presence of coordinated BF_3 or BF_4^- [10].

In contrast to the above situations in which the metal center acts as the Lewis base site, reaction of $(\eta^5\text{-}C_5Ph_4PPh_3)Mo(CO)_3$ with Al_2Me_6 resulted in an adduct in which a $AlMe_3$ had coordinated to a carbonyl oxygen atom (Fig. 18) [51]. Although no X-ray crystal structure data were reported, a CO stretching frequency of 1665 cm^{-1}, much lower in frequency than terminally bound carbonyls, is consistent with the reported carbonyl stretching frequency of $Cp_2Fe_2(CO)_4{\cdot}2AlEt_3$ (1682 cm^{-1}), which was shown by X-ray crystallography to have the $AlEt_3$ bound to carbonyl oxygen atoms [51]. It was suggested that equilibrium between free Al_2Me_6 and bound $AlMe_3$ in solution prevented the isolation and structural characterization of the pure compound.

The compounds $(\eta^5\text{-}C_5H_4PPh_3)M(CO)_3$ (M = Mo, W) were also found to react with HgX_2 (X = Cl, Br and I), CdI_2, $GaBr_3$ and $InBr_3$ (Fig. 19) [11,12]. In each of these examples, the Lewis acid was attached to the metal and not to a carbonyl oxygen, and in all cases 1:1 complexes were formed even in the presence of excess Lewis acid [11]. Satisfactory elemental analyses were obtained for most of the products but not all. In the case of, e.g. the $GaBr_3$ adduct of $(\eta^5\text{-}C_5H_4PPh_3)M(CO)_3$, starting material

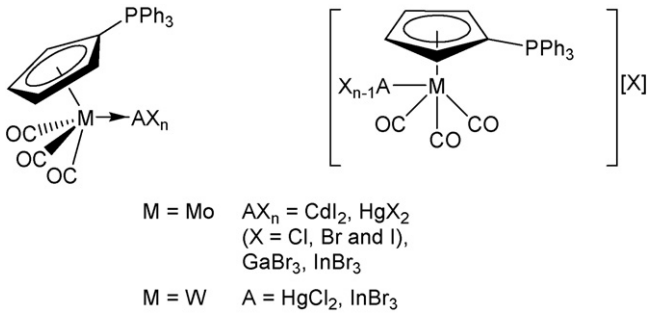

Fig. 19. The general structure of the Lewis acid-base adducts and the potential ionic complexes formed from these adducts.

was evident in the IR spectrum and all attempts to separate it from the Lewis acid-base adduct failed [11]. The IR spectra of these adducts were similar to those of the above-mentioned Lewis acid adducts reported by Kotz and Pedrotty, with CO stretching frequencies observed in the 2000–1870 cm^{-1} region [10].

Bonding of the Lewis acids to the CO oxygen was ruled out because of an absence of absorptions in the 1600 cm^{-1} region of the IR spectra [11]. With this group of Lewis acid-base adducts, the species could either be the neutral compounds or ionic complexes as shown in Fig. 19. Conductivity experiments done on the molybdenum complex of HgI_2 showed a molar conductance higher than expected for the neutral compound but lower than that expected for a 1:1 electrolyte. In addition, when $NaPF_6$ was added to the Mo:$InBr_3$ complex in an attempt to generate the PF_6^- salt, no reaction occurred [11]. Therefore, some ambiguity remains concerning the structures of these compounds.

The group 6 compounds $(\eta^5\text{-}C_5H_4PPh_3)M(CO)_3$ were also found by Cashman and Lalor to react with halogens and halogenating agents [11,12]. Reaction of a CH_2Cl_2 solution of the chromium compound with Br_2 at −70 °C resulted in a deep red solution which turned green on warming to −25 °C, but attempts to isolate a PF_6^- salt (via metathesis with $NaPF_6$) resulted in the isolation of the PF_6^- salt of the protonated ligand. In contrast, reactions of $(\eta^5\text{-}C_5H_4PPh_3)Mo(CO)_3$ with Cl_2, Br_2 and I_2 gave red compounds which were stable at room temperature and could be isolated. These were then converted to the PF_6^- salts by reaction with $NaPF_6$ [11], and the structure of the PF_6^- salt of the Mo–I_2 product is indicated in Fig. 20. Interestingly, the same compounds were obtained on reaction of $(\eta^5\text{-}C_5H_4PPh_3)M(CO)_3$ (M = Mo, W) with acetic acid to give the above-mentioned hydride compounds followed by halogenation with CCl_4 (Mo) and CBr_4 (Mo and W).

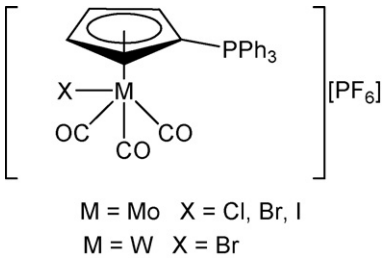

Fig. 20. The product of the reaction of the group 6 complexes by either direct halogenation or using a halogenting agent (i.e. CCl_4 or CBr_4).

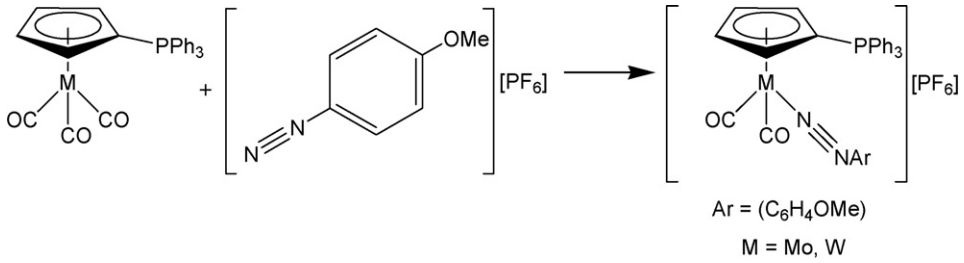

Fig. 21. The reaction of the group 6 complexes with *p*-anisyldiazonium hexafluorophosphate.

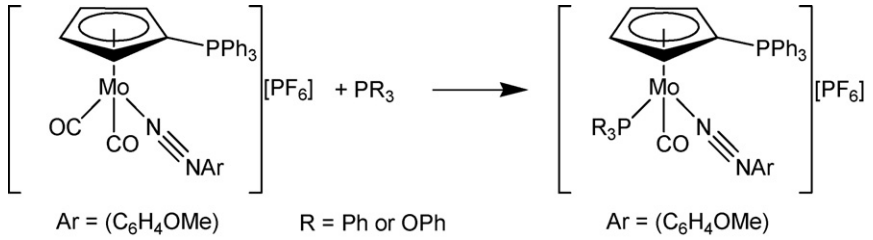

Fig. 22. CO displacement from the diazomolybdenum complex by PR_3.

The group 6 tricarbonyl complexes of $C_5H_4PPh_3$ and the molybdenum tricarbonyl complex of the tetraphenyl analogue, $C_5Ph_4PPh_3$, were reacted with *p*-anisyldiazonium hexafluorophosphate (Fig. 21) [11,12]. The reaction of (η^5-$C_5H_4PPh_3$)$Cr(CO)_3$ resulted in complete decomposition and gave the protonated ylide as the only characterizable product, but the molybdenum and tungsten compounds gave the arylazodicarbonyl metal complexes shown in greater than 90% yield. Reaction of the molybdenum compound with PPh_3 in refluxing THF also resulted in the substitution of one CO by PPh_3 to give the mono-carbonyl compound (Fig. 22) [11].

In view of the oxidation chemistry of the group 6 cyclopentadienyl tricarbonyl anions, $[CpM(CO)_3]^-$, the reaction of (η^5-$C_5Ph_4PPh_3$)$Mo(CO)_3$ with the oxidant, tris(*p*-bromophenyl)amminium hexachloroantimonate was examined by Cashman and Lalor [11]. An instantaneous reaction occurred, after which the resulting product was reacted with $NaPF_6$ to give $[(C_5H_4PPh_3)Mo(CO)_3Cl][PF_6]$ [11]. Performing the same reaction using the amminium perchlorate salt yielded the dimeric compound shown in Fig. 23, but, because of the potentially explosive nature of the perchlorate salt, elemental analyses were not performed. The poor solubility of this salt also prevented metathesis to the PF_6^- salt. The IR spectrum of the perchlorate dimer exhibited four carbonyl stretches (2058 (w), 2027 (m), 1981 (s) and 1930 cm^{-1} (s)) consistent with the suggested structure [11], and a compound with an almost identical IR spectrum was isolated when (η^5-$C_5Ph_4PPh_3$)$Mo(CO)_3$ was reacted with nitrosonium hexafluorophosphate in an attempt to obtain the nitrosyl compound. The analytical data for the product indicate that it is dimeric (Fig. 23) [11]. The reaction of the oxidized compound (generated from the nitrosonium salt) with $NaBH_4$, regenerated the tricarbonyl starting compound, and thus the nitrosonium salt was behaving as a one-electron oxidant.

Reaction of the molybdenum compound with liquid SO_2 or with SO_2 dissolved in CH_2Cl_2 gave deep red solutions which decomposed on standing to yield amorphous brown, carbonyl-free products [11]. Removal of the solvent from these reactions yielded a red solid which quickly turned yellow, providing the tricarbonyl starting compound. An IR spectrum obtained before complete decomposition occurred exhibited peaks at 2028, 1988 and 1968 cm^{-1} (in addition to peaks from the starting material), and the product of this reaction was suggested to be the Lewis acid-base adduct of SO_2 (Fig. 24).

Reactions of $C_5H_4PPh_3$ with group 6 metal compounds in higher oxidation states were reported by Nalesnik et al., who reacted the ylide with the halides of the group 6 metals [31]. The reaction of $C_5H_4PPh_3$ with WCl_6 gave a substance with apparent stoichiometry $(C_5H_4PPh_3)_2WCl_6$, and the structure proposed is shown in Fig. 25. The ^1H NMR spectrum of the product showed that the resonances of the C_5 ring protons had shifted considerably downfield to δ 8.57 from the δ 6.20 of the free ligand. In addition, the phenyl resonances had also shifted to lower field,

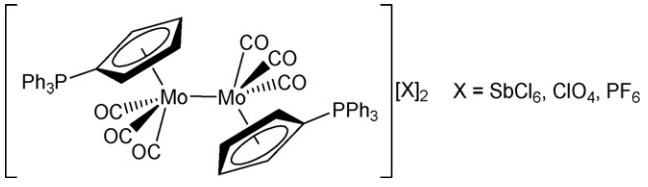

Fig. 23. The Mo–Mo bound dimer from the oxidation of the molybdenum complex.

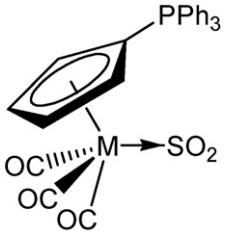

Fig. 24. The Lewis acid-base adduct of (η^5-$C_5H_4PPh_3$)$Mo(CO)_3$ and SO_2.

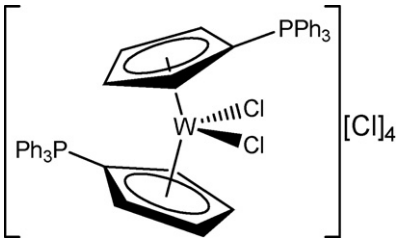

Fig. 25. The proposed structure of the compound obtained from the reaction of $C_5H_4PPh_3$ with WCl_6.

but to a much lesser extent. This deshielding would be expected on coordination of the ylide to a metal in such a high-oxidation state, but no crystal structure was obtained to substantiate the proposed structure [31]. $MoCl_5$ also reacted with $C_5H_4PPh_3$, giving a compound thought to be $(C_5H_4PPh_3)MoCl_3(OH)_2$ [31]; the hydroxides possibly resulted from traces of water in the solvents but the compound was not well characterized. Also reported was the reaction of $C_5H_4PPh_3$ with $CrCl_2$, but no product could be characterized.

Reactions of the chelating fluorenyl derived ylide based on bis(diphenylphosphino)methane, discussed above (Fig. 11), with $Cr(CO)_6$ and $W(CO)_3(CH_3CN)_3$ proceeded as shown in Fig. 26 [35]. The IR spectrum of the tungsten compound exhibited four CO stretching bands, similar to the previously reported spectrum of W(phen)$(CO)_4$ [35]. Further evidence of the suggested structure was given by the ^{31}P NMR spectrum, which exhibited the two phosphorus resonances which had shifted significantly downfield relative to the chemical shifts of the free ligand and consistent with bonding at both the ylidic carbon and the pendant-PPh_2 phosphorus. This was the first tungsten compound containing a cyclopentadienyl moiety bound in a monohapto manner.

The analogous reaction of $Cr(CO)_6$ yielded two products, one exhibiting IR and ^{31}P NMR spectra similar to those obtained for the tungsten compound, the second a compound which exhibited three CO bands in the IR spectrum. The ^{31}P NMR data showed that neither phosphorus resonance was greatly shifted, indicating that the likely structure was the compound in which the $Cr(CO)_3$ is bound to one of the C_6 rings of the fluorenyl group (Fig. 27) [35].

The group 6 metal complexes of $C_5H_4PMePh_2$, $(\eta^5$-$C_5H_4PPh_3)M(CO)_3$ (M = Cr, Mo, W), have been prepared much as were the corresponding complexes of $C_5H_4PPh_3$ (see Fig. 15). All have been characterized spectroscopically (IR; ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR) and crystallographically, and this series of compounds is one of the best characterized series of phosphonium cyclopentadienylide compounds available [37]. The compounds are η^5-bonded as in Fig. 28, and comparisons of ν(CO) of these compounds with those of the isoelectronic $(\eta^6$-$C_6H_6)M(CO)_3$ and $[(\eta^5$-$C_5H_5)M(CO)_3]^-$ suggest that the electron donating ability of the ylide is less than that of the cyclopentadienyl anion but much greater than that of benzene [37]. DFT calculations suggest that the primary ylide–metal interactions in $(\eta^5$-$C_5H_4PMePh_2)Cr(CO)_3$ involve donation of the HOMO and (HOMO-1) orbitals (Fig. 4) into the d_{xz} and d_{yz} orbitals of the chromium (Fig. 29), and that the ylide–$Cr(CO)_3$ bond dissociation energy is some 30% higher than the analogous ring-metal dissociation energy of the arene compound $(\eta^6$-$C_6H_6)Cr(CO)_3$.

Aspects of the chemistry of the compounds $(\eta^5$-$C_5H_4PMePh_2)M(CO)_3$ (M = Cr, Mo) have been investigated [37]. Thermal and photochemical reactions with equimolar amounts of PMe_3 and PPh_3 did not result, surprisingly, in CO substitution, but the ylide is displaced photochemically from $(\eta^5$-$C_5H_4PMePh_2)Mo(CO)_3$ by excess PMe_3 to form *fac*-$Mo(CO)_3(PMe_3)_3$. The com-

Fig. 27. The structure of the chromium complex with the metal bound to the fluorenyl phenyl ring.

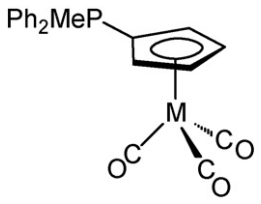

Fig. 28. Structure of the compounds $(\eta^5$-$C_5H_4PMePh_2)M(CO)_3$ (M = Cr, Mo, W).

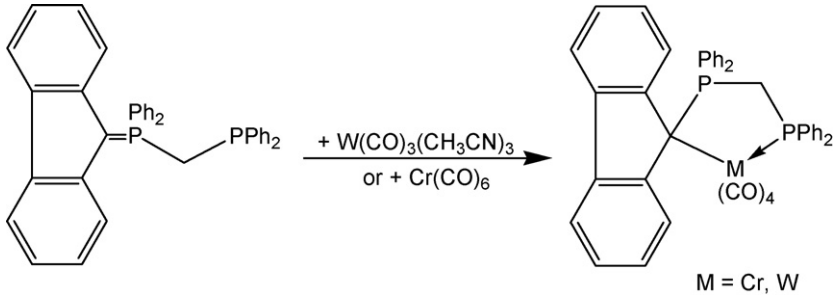

Fig. 26. The reaction of the chelating fluorenyl derived ylide with the group 6 metal starting materials $Cr(CO)_6$ and $W(CO)_3(CH_3CN)_3$.

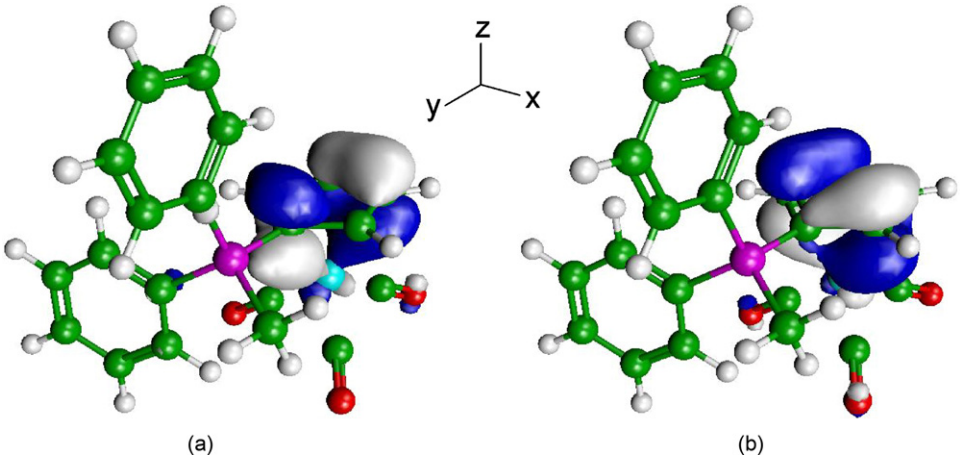

Fig. 29. Contour plots of the primary η^5-C_5H_4–Cr interactions in $(\eta^5\text{-}C_5H_4PMePh_2)Cr(CO)_3$, involving the d_{xz} (a) HOMO-4 and d_{yz} (b) HOMO-3 orbitals on Cr.

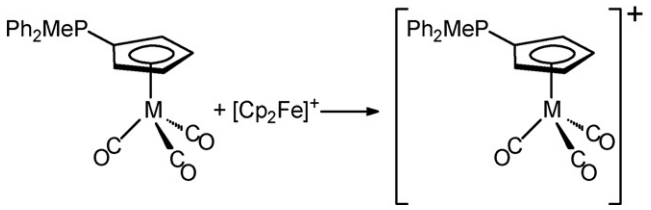

Fig. 30. One-electron oxidations of $M(\eta^5\text{-}C_5H_4PMePh_2)(CO)_3$ (M = Cr, Mo, W).

pound $(\eta^5\text{-}C_5H_4PMePh_2)Mo(CO)_3$ reacts with I_2 to form $[(\eta^5\text{-}C_5H_4PMePh_2)Mo(CO)_3I]I$ which has been characterized spectroscopically (IR, ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR) and crystallographically [37]. This behaviour is, of course, similar to that discussed above for the compounds $(\eta^5\text{-}C_5H_4PPh_3)Mo(CO)_3$ [11].

Electrochemical oxidations of the compounds $M(\eta^5\text{-}C_5H_4PMePh_2)(CO)_3$ (M = Cr, Mo W) occur via one-electron processes at potentials which are highly positive of the values previously observed for the analogous 18-electron anions $[M(\eta^5\text{-}C_5H_5)(CO)_3]^-$ [38]. On the basis of the experimentally determined oxidation potentials and observations that the oxidized species were long-lived, bulk oxidations of $M(\eta^5\text{-}C_5H_4PMePh_2)(CO)_3$ (M = Cr, Mo W) by $[FeCp_2][B(C_6F_5)_4]$ were carried out to give initially the cationic radical species $[M(\eta^5\text{-}C_5H_4PMePh_2)(CO)_3]^+$ (Fig. 30), which in turn dimerized to give the crystalline products $\{[M(\eta^5\text{-}C_5H_4PMePh_2)(CO)_3]_2\}^{2+}$, shown in Fig. 31. The latter were isolated analytically pure and were characterized by IR (solid state and solution) and NMR (^1H, ^{13}C, ^{19}F and

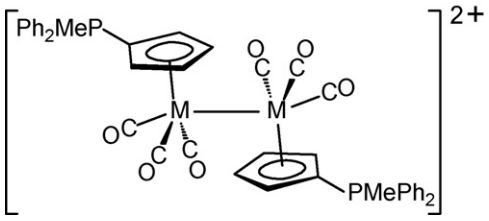

Fig. 31. The dimers, $[M(\eta^5\text{-}C_5H_4PMePh_2)(CO)_3]_2^{2+}$.

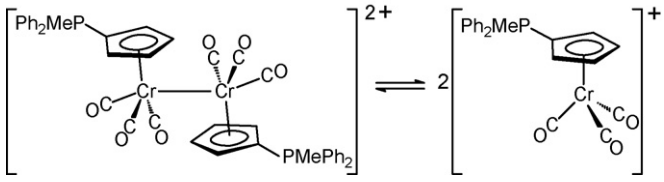

Fig. 32. Monomer-dimer equilibrium for the chromium cation radical system.

^{31}P) spectroscopy, high-resolution mass spectrometry and crystallographically. The dimers all contain metal–metal bonds which are comparable in length with or longer than the metal–metal bonds in the isoelectronic, neutral η^5-C_5H_5 and η^5-C_5Me_5 analogues, and the metal–metal bond in $[Cr(\eta^5\text{-}C_5H_4PMePh_2)(CO)_3]_2[B(C_6F_5)_4]_2$ is the longest non-bridged Cr–Cr bond known. As a result of the apparent weakness of its Cr–Cr bond, $\{[Cr(\eta^5\text{-}C_5H_4PMePh_2)(CO)_3]_2\}^{2+}$ dissociates significantly in solution to the paramagnetic radical cation (Fig. 32) [38].

2.3. Group 7 metals

Two literature reports discuss syntheses of group 7 metal compounds. In 1976, Nesmeyanov et al. [16] reported the synthesis of a cationic manganese tricarbonyl complex of $C_5H_4PPh_3$. When $C_5H_4PPh_3$ was stirred for 1 day at room temperature with $[Mn(CO)_3(CH_3CN)_3][PF_6]$ in either THF or diglyme, $[(\eta^5\text{-}C_5H_4PPh_3)Mn(CO)_3][PF_6]$ was synthesized as shown in Fig. 33 [16]. This compound is isoelectronic with the group 6 compound $(\eta^5\text{-}C_5H_4PPh_3)Cr(CO)_3$, is stable in air as a solid and is soluble in polar solvents such as acetone, THF, methanol and ethanol. Characterization was carried out using IR and ^1H NMR spectroscopy, mass spectrometry (MS) and elemental analyses. Two carbonyl stretching modes were observed in the IR spectrum at 1963 and 2040 cm^{-1}, consistent with

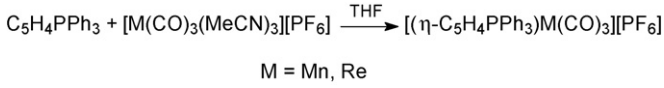

Fig. 33. The synthesis of $[Mn(CO)_3(CH_3CN)_3][PF_6]$ (M = Mn, Re).

the proposed structure. The ^{1}H NMR spectrum in acetone-d_6 exhibits one resonance for the C_5 ring protons at δ 5.83 and a resonance at δ 8.11 for the phenyl protons. Using EI–MS, the parent ion was that of the ionized ylide ($m/z = 326$), not the molecular ion, indicating fragmentation of the manganese compound. In addition, heating was required to achieve sufficient volatilization of the sample and this may have resulted in thermal degradation.

In a separate report by the same group, the synthesis of the analogous rhenium tricarbonyl compound was described [17]. The ^{1}H NMR spectrum of this exhibited resonances at δ 6.27 (C_5 ring protons) and at δ 7.92 (phenyl protons), while the IR spectrum exhibited two carbonyl stretching bands at 2038 and 1950 cm^{-1}. As with the manganese compound, the MS spectrum of the rhenium compound did not exhibit a molecular ion peak, again most likely because of thermal degradation. ^{13}C NMR data were collected for both the manganese and rhenium compounds, and for both the P–C carbon of the C_5 ring was only slightly shielded relative to the free ligand. A much more dramatic shift was observed for the other carbon resonances of the C_5 ring, which were shifted upfield by more than 20 ppm for both compounds [17]. As expected, little change was noted in the phenyl carbon resonances.

No investigation into the reactivities of these compounds has been reported, leaving a large hole in understanding the behaviour of such species. In addition, while the spectroscopic data clearly indicate successful syntheses of the desired compounds, no structural information was presented. Both compounds were reported as being highly crystalline [16,17] and X-ray structures of these compounds should be possible and would add to the understanding of their bonding.

2.4. Group 8 metals

Syntheses of iron complexes of phosphonium cyclopentadienylides have been accomplished using two distinctly different methodologies. As in other cases, the direct reaction of $C_5H_4PPh_3$ with several iron precursors has been reported, but, in addition, a completely new synthetic pathway using the quaternization of ferrocenyl phosphines has been developed.

The reaction of $C_5H_4PPh_3$ with $Fe(CO)_5$ was initially reported by Cashman and Lalor [11]. When $Fe(CO)_5$ was refluxed with $C_5H_4PPh_3$ in dimethoxyethane in an attempt to synthesize the compound shown in Fig. 34, 65% of the ligand was recovered unreacted. Column chromatography yielded a very small amount of a yellow crystalline iron carbonyl product for which four carbonyl stretching bands in the IR spectrum were observed, but the limited quantity of material actually obtained was insufficient to allow further characterization [11]. Alper and Partis [52] subsequently reported that the reaction of $Fe_2(CO)_9$ with $C_5H_4PPh_3$ gave an unstable red product which exhibited IR bands in the same region (2049, 1993, 1970 and 1934 cm^{-1}) as the compound reported by Cashman and Lalor [11], but further examination of the product seems not to have been carried out. Alper and Partis also reacted the fluorenyl derived ylide of triphenylphosphine (Fig. 10) with $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$, but did not obtain any organometallic product; only the olefin, bis-fluorenylidine was isolated in a 10% yield [52].

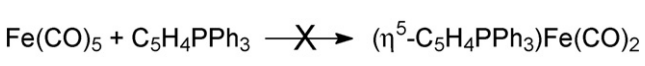

Fig. 34. The attempted reaction of $C_5H_4PPh_3$ with $Fe(CO)_5$.

When $C_5H_4PPh_3$ was stirred with $FeCl_2$ in THF for several days, there was obtained a brown precipitate which, from elemental analyses, had a stoichiometry of $(C_5H_4PPh_3)Fe_2Cl_4$ [32]. The compound was stable at room temperature, slightly air-sensitive and soluble only in coordinating solvents such as DMF and DMSO. A ^{31}P NMR spectrum of the material in DMF exhibited a single sharp resonance at δ 25.9, the sharpness of the peak being taken as evidence of diamagnetism of the compound [32]. On the addition of pentane to the filtrate from this reaction, a dark red, highly air-sensitive compound was obtained. The ^{31}P NMR spectrum of this in THF-d_8 exhibited only a single resonance at δ 13.2, nearly identical to that of the starting ylide (δ 13.1 in $CDCl_3$), while elemental analyses revealed that the product had a stoichiometry of $(C_5H_4PPh_3)_3Fe_2Cl_4$. Unfortunately, for neither product were ^{1}H NMR data obtained.

A second synthetic route to iron phosphonium cyclopentadienylides was reported in 1963 by Sollot et al. [53]. In this method, methyl iodide was added to ferrocenes containing phosphine substituted Cp rings (ferrocenyl phosphines) to quaternize the phosphine and give the ionic ylide compounds shown in Fig. 35. These were characterized by elemental analyses and IR spectroscopy, and are structurally related to $C_5H_4PPh_3$ and the above-mentioned ansa-zirconocene and -hafnocene complexes of phosphonium bridged permethylcyclopentadienyl ligands (Figs. 12–14) [50] although these parallels were not drawn.

Other reports examined similar protocols to generate phosphonium salts of ferrocene derivatives. In 1976, in the course of an examination of the kinetics of quaternization of a variety of phosphines and arsines, McEwen et al. synthesized several benzyl derivatives of ferrocenes via the addition of benzyl choride to ferrocenyl phosphines to give benzyldiphenylferrocenylphosphonium chloride and benzylphenyldiferrocenylphosphonium chloride, as shown in Fig. 36 [54]. A crystal structure of one of these Ramirez ylide-type complexes was also reported [55], and the P–C_5 bond length was found to be 1.768(3) Å, similar to those in other coordination compounds of Ramirez type ylides and shorter than a P–C single bond.

A much later report, published in 1994, examined substituent effects on the synthesis of benzyldiphenylferrocenylphosphonium salts by addition of benzyl halides to diphenylferrocenylphosphines, followed by conversion to the BF_4^- salts to yield a series of *para*-substituted benzyl complexes (Fig. 37) [56]. The crystal structure of the methoxy derivative was reported, as well as extensive spectroscopic characterization, making these some of the best characterized examples of this class of compounds. The crystal structure of 4-methoxybenzyldiphenylferrocenylphosphonium tetrafluoroborate is very similar to that of benzyldiphenylferrocenylphosphonium chloride, with a similar P–C_5 bond length [56].

Several examples of ruthenium complexes have also been reported for $C_5H_4PPh_3$. In 1995, the reaction of the cluster compound $Ru_6C(CO)_{17}$ with $C_5H_4PPh_3$ in the presence of the

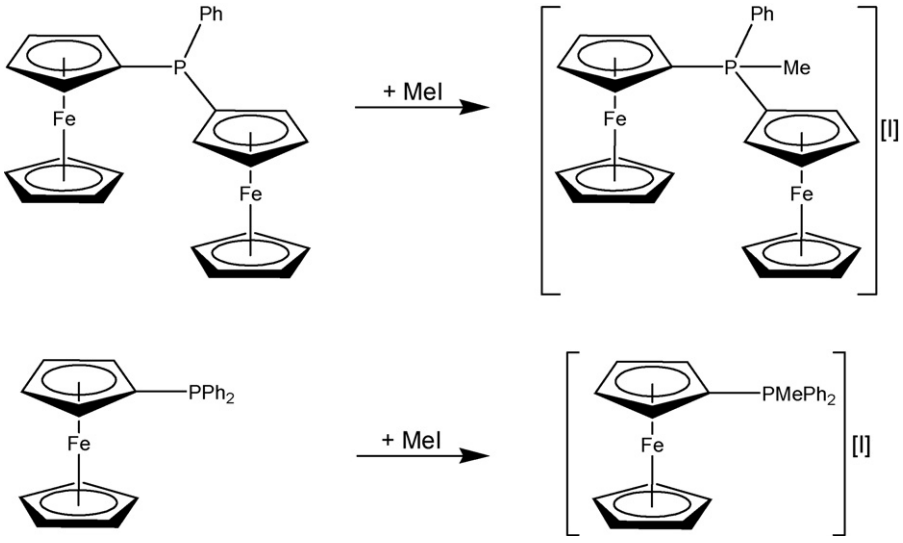

Fig. 35. Synthesis of iron ylide complexes by quaternization of ferrocenyl phosphines.

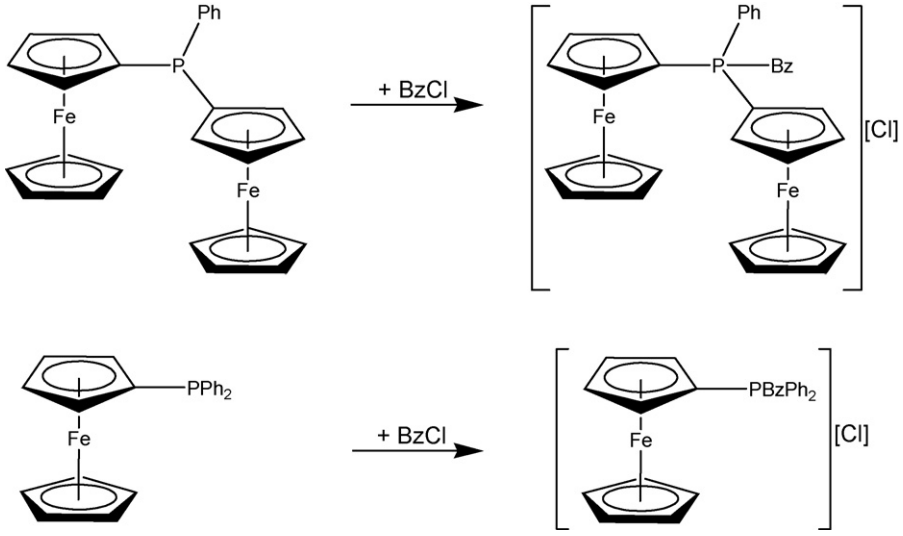

Fig. 36. Synthesis of iron ylide complexes by quaternization of ferrocenyl phosphines using benzyl chloride.

decarbonylating agent trimethylamine N-oxide was found to yield the compound $Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_4PPh_3)$ [20]. The latter compound was obtained in moderate yield (64%), and was characterized by IR and ^1H and ^{31}P NMR spectroscopy, MS and X-ray crystallography. The crystal structure confirmed that the ylide was bound in an η^5 manner, as in Fig. 38 [20]. The P–C_5 bond length of 1.793(12) Å is considerable longer than in free $C_5H_4PPh_3$ (1.718(2) Å [7], as is more akin to a P–C single bond, while the P–C_5 bond is bent significantly out of the plane of the C_5 ring by 19.4(6)°. The major CO stretching band in the IR spectrum is lower in frequency than that of $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$ by 17 cm^{-1}, indicating that the ylide is a better electron donor than is benzene.

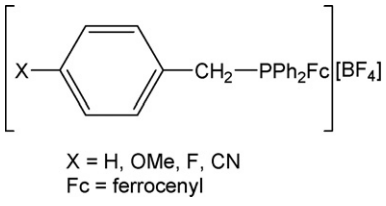

Fig. 37. Various *para*-substituted benzyl derivatives of diphenylferrocenylphosphonium.

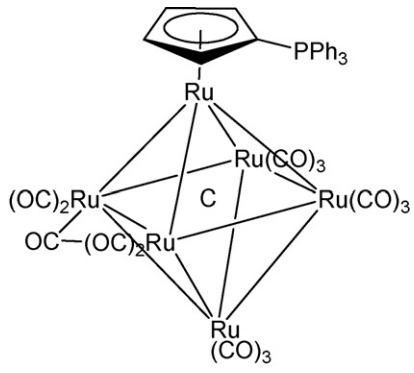

Fig. 38. The structure of $Ru_6C(CO)_{14}(\eta^5\text{-}C_5H_4PPh_3)$.

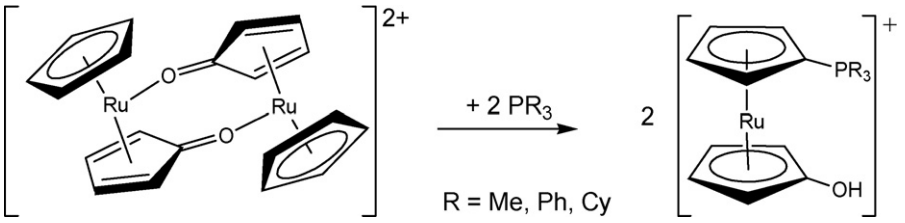

Fig. 39. Reaction of phosphines with $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)]_2[PF_6]_2$.

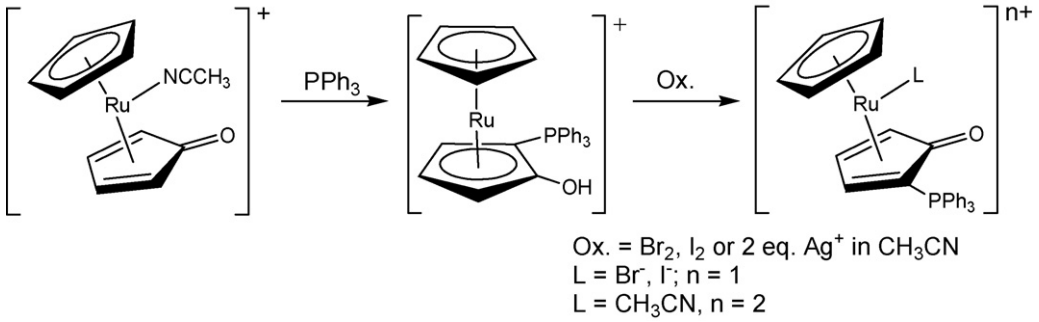

Fig. 40. The reaction of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(CH_3CN)][PF_6]$ with PPh_3 and the resulting products of oxidation.

Two other interesting reports describe reactions of ruthenium compounds which result in the formation of phosphonium cyclopentadienylide complexes. The first report described the reaction of the compound $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4O)]_2[PF_6]_2$ with a variety of nucleophiles, including several phosphines which gave the products shown in Fig. 39 [57]. The products were isolated in 50–60% yield for the phosphines PR_3 (R = Me, Cy, Ph), but appeared to be quantitative when carried out on an NMR scale. A crystal structure of the tricyclohexylphosphine derivative was obtained and showed a P–C_5 bond length of 1.790(3) Å, typical of complexes with similar ylide ligands.

Similar chemistry was observed when PMe_3 and PCy_3 were reacted with $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(CH_3CN)][PF_6]$, but, when PPh_3 was used, substitution of the cyclopentadienone occurred to give the ylide compound $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3OH\text{-}2\text{-}PPh_3)][PF_6]$, shown in Fig. 40 [57]. The latter compound was found to undergo oxidation by Br_2, I_2 and Ag^+ in CH_3CN to yield the phosphine substituted cyclopentadienone Ru compound [57].

When $[CpRuFvRuCp][BF_4]_2$ (Fv, fulvalene) was reacted with an excess of PPh_3, the 1'-substituted biruthenocene shown in Fig. 41 was formed as the major product (87%) [58]. The X-ray crystal structure confirmed the ylide structure, the P–C_5 bond length of 1.769(3) Å being longer than in $C_5H_4PPh_3$ but shorter than a P–C single bond. The ^{31}P NMR resonance was observed at δ 25.08, in the region expected for the coordination complex of $C_5H_4PPh_3$ [58] although, again, there was no parallel made with known Ramirez ylide-types of compounds.

An interesting paper describes a reaction in which $C_5H_4PPh_3$ was found to oxidatively add one of the C_5 ring C–H bonds to $Os_3(CO)_{10}(MeCN)_2$ to give $Os_3(\mu\text{-}H)(\mu\text{-}C_5H_3PPh_3)(CO)_{10}$; in this compound, the C_5 ring was bound to two osmium atoms through a single carbon atom (Fig. 42) [59]. The compound exists in solution as an equilibrium mixture of two isomers, as in Fig. 43, and a crystal structure was obtained for isomer (**A**). The crystal structure revealed a P–C_5 bond length of 1.74(2) Å which is just slightly longer than in $C_5H_4PPh_3$ and is another indication that the dominant contribution to the bonding situation is made by the zwitterionic resonance structure. The pure

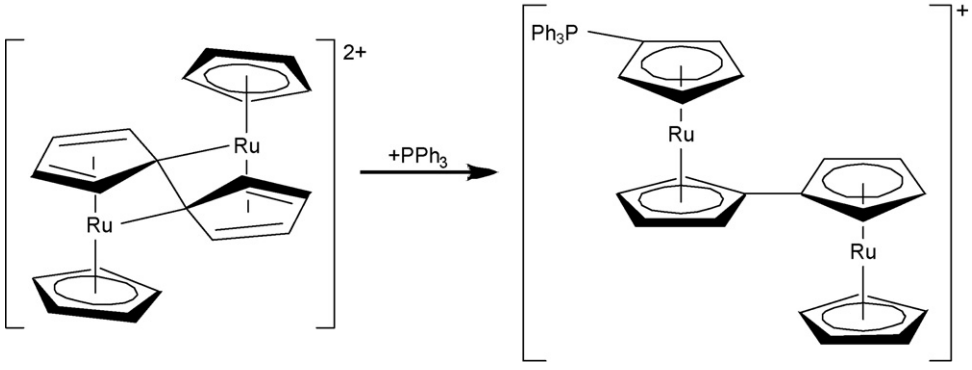

Fig. 41. The reaction of $[CpRuFvRuCp][BF_4]_2$ with PPh_3.

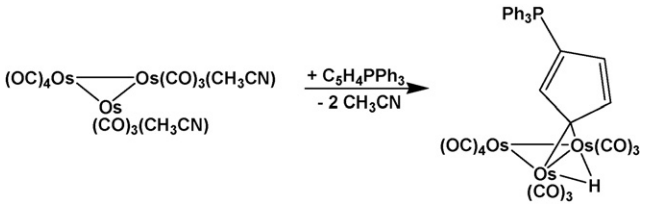

Fig. 42. The reaction of $Os_3(CO)_{10}(MeCN)_2$ with $C_5H_4PPh_3$.

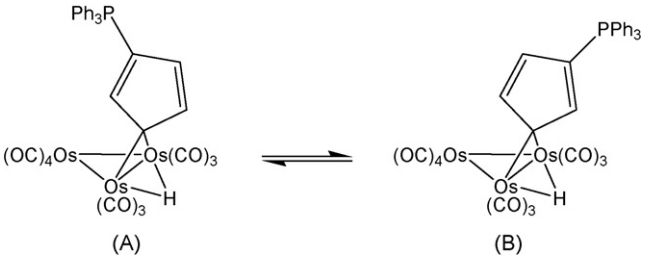

Fig. 43. Isomerization of $Os_3(\mu\text{-}H)(\mu\text{-}C_5H_3PPh_3)(CO)_{10}$.

isomer (**B**) was isolated by chromatography, and the IR spectra of the two isomers were found to be indistinguishable, the ^1H NMR spectra were very similar. A mechanism for the isomerization was proposed, but experiments designed to support the proposal did not yield conclusive results [59].

When (**A**) or mixtures of (**A**) and (**B**) were heated in refluxing toluene, two isomers of the product of decarbonylation, $Os_3(\mu\text{-}H)(\mu_3\text{-}C_5H_3PPh_3)(CO)_9$, were obtained [59]. The crystal structure of one of the isomers revealed that the C_5H_3 ring had adopted an μ_3 structure, bridging the three osmium atoms of the cluster. The ligand can be thought of as donating four electrons through two sigma bonds and two electrons through one η^2 bond of a C_5 ring double bond. The two isomers are shown in Fig. 44.

2.5. Group 9 metals

The first report of group 9 metal complexes of phosphonium cyclopentadienylides appeared in 1978, when Holy et al. reported the synthesis and structure of the compound $[(\eta^5\text{-}C_5H_4PPh_3)Co(CO)_2][Co(CO)_4]$ and its use to catalyze cyclotrimerization of alkynes to benzene derivatives [18]. The compound was synthesized by reacting $Co_2(CO)_8$ with $C_5H_4PPh_3$ in THF (Fig. 45) [18], and was isolated in 65% yield. A crystal structure showed similarities to other structures of this class of compound [18,19]; the C_5 ring is bound in an η^5 manner, and the P–C_5 bond showed typical elongation (1.765(6) Å) on coordination to the cobalt.

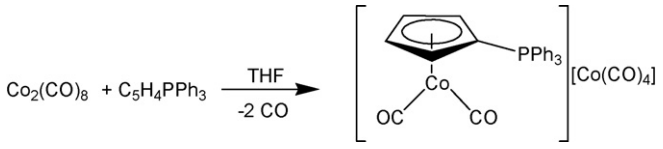

Fig. 45. The synthesis of $[(\eta^5\text{-}C_5H_4PPh_3)Co(CO)_2][Co(CO)_4]$.

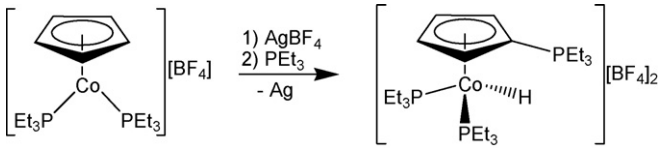

Fig. 46. The synthesis of $[CpCo(PEt_3)_2][BF_4]$.

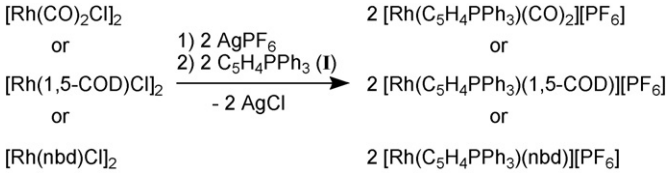

Fig. 47. The synthesis of Rh(I) complexes of $C_5H_4PPh_3$.

A cobalt(III) complex of a Ramirez type ylide was obtained as the unexpected product of the reaction of $[CpCo(PEt_3)_2][BF_4]$ with one equivalent of $AgBF_4$, followed by the addition of one equivalent of PEt_3 (Fig. 46) [60]. The product, $[(C_5H_4PEt_3)CoH(PEt_3)_2][BF_4]_2$, was obtained in 88% yield. Confirmation of this formulation was provided by the ^1H NMR spectrum which exhibited two multiplets for the C_5H_4 ring protons at δ 6.3 and 5.6 and a hydride resonance at −15.4, and elemental analyses, but crystallographic information was not obtained.

The first reports of rhodium complexes of $C_5H_4PPh_3$ appeared in 1981 by Tresoldi et al. [21] who synthesized a series of Rh(I) and Rh(III) complexes. The reactions of $[Rh(CO)_2Cl]_2$, $[Rh(1,5\text{-}COD)Cl]_2$ and $[Rh(nbd)Cl]_2$ (nbd, norbornadiene) with $AgPF_6$ followed by addition of $C_5H_4PPh_3$ resulted in the syntheses of $[Rh(C_5H_4PPh_3)(CO)_2][PF_6]$, $[Rh(C_5H_4PPh_3)(1,5\text{-}COD)][PF_6]$ and $[Rh(C_5H_4PPh_3)(nbd)][PF_6]$, respectively (as shown in Fig. 47) [21]. In contrast, $C_5H_4PPh_3$ behaves as a poor nucleophile and was found not to cleave the chloro-bridged dimers. The compounds exhibited good solubilities in acetone and DMSO, were slightly soluble in CH_2Cl_2 and MeOH and

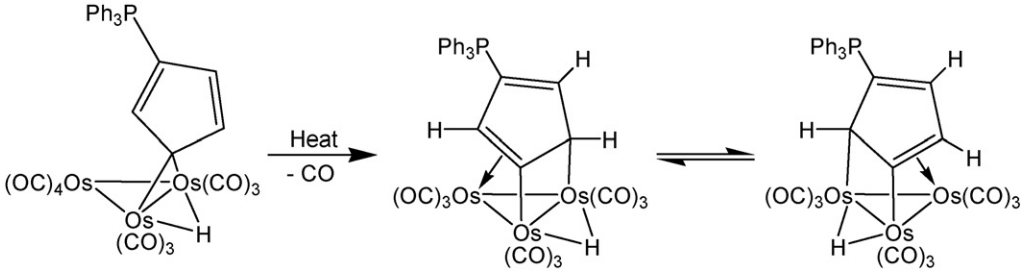

Fig. 44. The product and isomerization of the decarbonylation of $Os_3(\mu\text{-}H)(\mu\text{-}C_5H_3PPh_3)(CO)_{10}$.

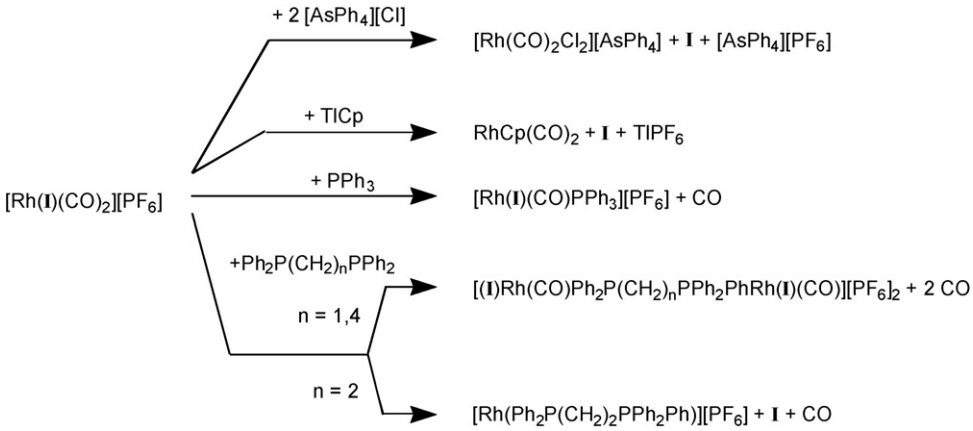

Fig. 48. The reactions of $[Rh(C_5H_4PPh_3)(CO)_2][PF_6]$.

insoluble in non-polar solvents such as benzene. They were characterized by ^1H and ^{13}C NMR and IR spectroscopy. The IR spectrum of $[Rh(C_5H_4PPh_3)(CO)_2][PF_6]$ exhibited carbonyl stretches at higher frequencies than for the corresponding Cp complex, providing further evidence that $C_5H_4PPh_3$ is not as good a donor as Cp. A crystal structure of the tetraphenylborate salt of $[Rh(C_5H_4PPh_3)(1,5\text{-COD})]^+$ was reported later by the same group [27]. The crystal structure revealed that, as expected, $C_5H_4PPh_3$ was bound in an η^5 manner, with Rh–C_5 bond lengths of 2.22(1)–2.29(1) Å and a P–C_5 bond length of 1.76(1) Å.

Substitution chemistry of $[Rh(C_5H_4PPh_3)(CO)_2][PF_6]$ was also examined by this group [21]. Reactions of $[Rh(C_5H_4PPh_3)(CO)_2][PF_6]$ with [AsPh4]Cl or TlCp resulted in displacement of the $C_5H_4PPh_3$ and formation of $[Rh(CO)_2Cl_2][AsPh_4]$ or $Rh(Cp)(CO)_2$, respectively (Fig. 48) [21]. In contrast, reaction of $[Rh(C_5H_4PPh_3)(CO)_2][PF_6]$ with PPh_3 resulted in the displacement of one carbonyl by the phosphine to yield $[Rh(C_5H_4PPh_3)(CO)PPh_3][PF_6]$. The mechanism and kinetics of the CO displacement by PPh_3 in this compound were further studied by Rerek and Basolo who found that CO substitution occurred ~100 times faster than in the corresponding Cp compound [61].

The reactions of $[Rh(C_5H_4PPh_3)(CO)_2][PF_6]$ with the diphosphines, $Ph_2P(CH_2)_nPPh_2$ ($n=1$ (dppm), 2 (dppe), 4 (dppb)) were also studied, dppm and dppb giving the phosphine–bridged compounds $[Rh(C_5H_4PPh_3)(CO)(\mu\text{-dppm})Rh(C_5H_4PPh_3)(CO)][PF_6]_2$ and $[Rh(C_5H_4PPh_3)(CO)(\mu\text{-dppb})Rh(C_5H_4PPh_3)(CO)][PF_6]_2$ (Fig. 48) [21]. However, when dppe was reacted with $[Rh(C_5H_4PPh_3)(CO)_2][PF_6]$, both $C_5H_4PPh_3$ and the carbonyl ligands were displaced to give $[Rh(dppe)_2][PF_6]$. The reaction of $[Rh(Cp^*)(acetone)_3][PF_6]_2$ with $C_5H_4PPh_3$ yielded the sandwich complex, $[Rh(Cp^*)(C_5H_4PPh_3)][PF_6]_2$ in 78% yield (Fig. 49), the compound being characterized by elemental analyses, and ^1H and ^{13}C NMR spectroscopy. In contrast to the other compounds of rhodium discussed above, the ^1H NMR spectrum of this sandwich complex exhibited only a single multiplet resonance for the C_5H_4 ring protons [21].

As part of a study on the cyclotrimerization of acetylenes catalyzed by various η^5-CpRh compounds, the compound $[Rh(C_5H_4PPh_3)(CO)_2][PF_6]$ was examined for its ability to trimerize dimethylacetylenedicarboxylate (DMAD) and 3-hexyne [62]. The rates of cyclotrimerization of DMAD varied in the order $[Rh(C_5H_4PPh_3)(CO)_2][PF_6] < \eta^5\text{-CpRh(CO)}_2 < \eta^5\text{-Cp*Rh(CO)}_2$, but all rates were in the same order of magnitude. In the trimerization of 3-hexyne, $[Rh(C_5H_4PPh_3)(CO)_2][PF_6]$ again proved to exhibit the lowest catalytic activity of the catalysts in this group.

The cobalt and rhodium complexes discussed above provide the first and, to date, the only examples of the use of Ramirez ylide-derived metal complexes as catalysts [18,62]. With the importance of metallocene catalysts in a variety of applications, it is surprising that so few reports of catalysis using Ramirez-derived complexes exist.

2.6. Group 10 metals

Only one report in the literature details the synthesis of nickel complexes of phosphonium cyclopentadienylides, Booth and Smith reporting in 1981 that $C_5H_4PPh_3$ reacts with nickelocene or $NiBr_2$, followed by the addition of NH_4PF_6, to give the apparent sandwich complex $[Ni(C_5H_4PPh_3)_2][PF_6]_2$, shown in Fig. 50 [23]. The ^1H NMR spectrum of this purple compound exhibited a multiplet at δ 7.72, attributed to overlapping C_5H_4 and phenyl resonances, while the ^{31}P NMR spectrum exhibited a

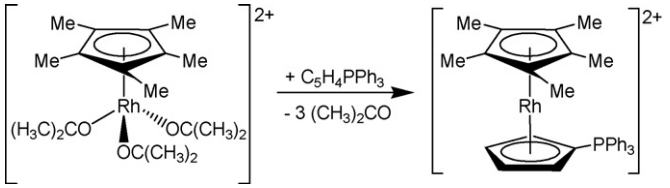

Fig. 49. The synthesis of the sandwich complex $[Rh(Cp^*)(C_5H_4PPh_3)][PF_6]_2$.

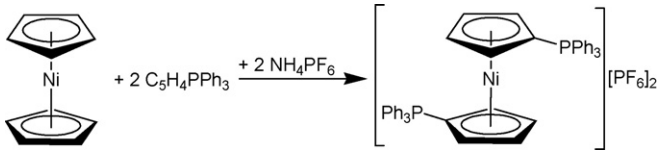

Fig. 50. Reaction of nickelocene with $C_5H_4PPh_3$.

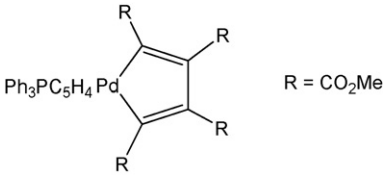

Fig. 51. The structure of the complex $(C_5H_4PPh_3)Pd(C_4(CO_2Me_4)$.

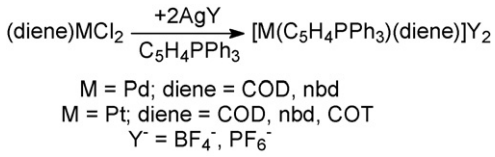

Fig. 52. The synthesis of cationic palladium and platinum diene complexes of $C_5H_4PPh_3$.

septet resonance attributed to the counteranion, PF_6^- (δ 144.7) and two singlets, a strong resonance at δ −15.6 and a much weaker resonance at δ 11.7. The apparent observation of two phosphonium ^{31}P resonances was thought to imply the presence of two rotamers of the η^5-bound ylidic rings, but this explanation seems unreasonable as hindered rotation is unlikely for this molecule. However, the solubility of the compound was very poor and it was suggested that the observed resonances may well result from impurities. Another problem, of course, is that if the compound is indeed the suggested sandwich complex, it would be isoelectronic with nickelocene and therefore quite likely paramagnetic and would presumably exhibit broadened resonances. This factor was not considered, nor were magnetic measurements made.

In addition to the above, the reactions of $C_5H_4PPh_3$ with $NiX_2(PPh_3)_2$ (X = Br, I) were also examined [23]. On stirring in chloroform, mixtures of $NiX_2(PPh_3)_2$ (X = Br, I) and $C_5H_4PPh_3$ gave deep violet solutions which yielded $[Ni(C_5H_4PPh_3)(PPh_3)_2][PF_6]_2$ on the addition of NH_4PF_6. The ^1H NMR again showed only a multiplet centered at δ 7.44 but no ^{31}P NMR data were provided.

The first report of a palladium complex of $C_5H_4PPh_3$ appeared in 1976 [24]. On reaction of $C_5H_4PPh_3$ with oligomeric $[PdC_4(CO_2Me)_4]_n$, the monomeric compound $(C_5H_4PPh_3)Pd[C_4(CO_2Me)_4]$ (Fig. 51) was obtained in 79% yield. ^1H NMR data and X-ray crystallography were provided to support this assignment. The ^1H NMR spectrum exhibits two sextets at δ 5.58 and 6.15, the difference between the shifts being greater than that observed for complexes of the group 6 tricarbonyl complexes. Pierpont et al. interpreted this to mean that the coordination of the C_5 ring was inconsistent with η^5 bonding [24], and a low temperature NMR spectrum was performed at −97 °C. At the lower temperature, the resonances of the C_5 ring protons converged somewhat, possibly indicating fluxionality of the bound ylide in the compound although this could not be proved. The crystal structure of this compound revealed that the Pd atom was bound asymmetrically to the C_5 ring of the ylide, the ylidic carbon atom and the adjacent carbon atoms having longer bond distances (2.447(6) and 2.429(6) Å) to the palladium atom than the other three carbons of the C_5 ring (2.399(6), 2.334(6) and 2.340 (6) Å) [24]. The P–C_5 bond length (1.776(9) Å) was elongated relative to the free ylide, and the bond lengths of the C_5 ring were also elongated relative to $C_5H_4PPh_3$. The C_5 ring bond lengths indicate some localization of single and double bond character, with some bond lengths approaching that of a C–C single bond (C(2)–C(3) = 1.47(1) Å, C(1)–C(5) = 1.46(1) Å). This was taken to indicate a degree of localized coordination. However, similar bond elongation and localization behaviour is seen in other compounds in which the C_5 ring is bound in an η^5 coordination mode [15,19] and the suggestion that this compound was the first in which the ylide $C_5H_4PPh_3$ was bound in an η^3 manner is not convincing. The Pd–C_5 ring distances are all sufficiently similar to indicate some type of bonding interaction with all carbons of the C_5 ring and the differences in Pd–C_5 bond lengths may be an artefact of steric interactions with the other palladium ligand.

Several palladium phosphonium cyclopentadienylide complexes were subsequently reported by Hirai et al. in two papers which appeared in 1979 [25,26]. Cationic palladium diene (1,5-COD or nbd) complexes were prepared *in situ* by the reaction of $(diene)PdCl_2$ with two equivalents of $AgBF_4$ (or other similar silver salts) [26]. These cationic compounds were then reacted with $C_5H_4PPh_3$ to furnish the compounds $[(\eta^5\text{-}C_5H_4PPh_3)Pd(diene)][BF_4]_2$ (53% yield for 1,5-COD and 64% for nbd) (Fig. 52). For these compounds, the ^1H NMR spectra revealed much smaller differences in the chemical shifts of the C_5 ring protons (0.22 ppm for 1,5-COD and 0 ppm for nbd) than was observed in the compound $(C_5H_4PPh_3)Pd[C_4(CO_2Me)_4]$. The PF_6^- salts of the same compounds were also later reported by Tresoldi et al. [22], and the method was also extended by Hirai et al. to allylic phosphonium cyclopentadienylide and allylic compounds shown in Fig. 53 [25]. Moderate to good yields (53–79%) were obtained for all compounds. ^1H NMR data and elemental analyses are consistent with the suggested structures [25].

Tresoldi et al. also reported the synthesis of platinum diene complexes of $C_5H_4PPh_3$ [22]. Using an identical procedure to that of Hirai et al. [26], the solvated $[Pt(diene)][PF_6]_2$ species (diene = 1,5-COD, nbd and 1,5-cyclooctatetraene (COT)) were prepared *in situ* and reacted with $C_5H_4PPh_3$ (Fig. 52) [22]. The resulting compounds, $[(\eta^5\text{-}C_5H_4PPh_3)Pt(diene)][PF_6]_2$, were obtained in yields ranging from 58 to 72%. Based upon ^1H NMR chemical shifts, all three compounds have $C_5H_4PPh_3$ bound to the Pt in an η^5 manner [22]. In solution, these compounds slowly lose diene. Attempts to prepare the methoxy derivative of the Pd or Pt compounds by reaction of $C_5H_4PPh_3$ with $[M(diene\text{-}OCH_3)(acetone)_2]^+$, or by the treatment of the dica-

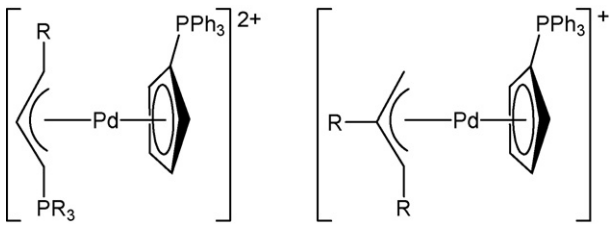

Fig. 53. Palladium allyl ylide and allyl complexes of $C_5H_4PPh_3$.

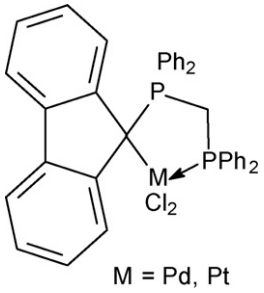

Fig. 54. Palladium and platinum complexes of the chelating fluorenyl ylide.

tionic compounds with base in the presence of methanol, failed [22].

Reactions of $Pd(PPh_3)_2Cl_2$ with the chelating 'fluorenyl' phosphonium ylides shown in Fig. 11 ($n = 1,2$) were reported by Holy et al. [35]. When $n = 1$, a compound with a structure similar to that reported for the chromium and tungsten compounds (Fig. 26) was obtained and is shown in Fig. 54. IR and ^1H and ^{31}P NMR data were reported for the compound, supporting the structure depicted in Fig. 54. The ^{31}P NMR spectrum exhibited an AB quartet (J 59.0 Hz) for the two phosphorus atoms, similar to the spectral data reported for compounds of chromium and tungsten with similar coordination modes, and the IR spectrum exhibited two broad bands at 368 and 292 cm^{-1}, which are typical for *cis*-$PdCl_2$ units [35]. This work was also extended to platinum; $PtCl_2$ was reacted with the chelating 'fluorenyl' phosphonium ylide ($n = 1$) to provide a compound of the type shown in Fig. 54. This structural assignment was supported by the ^{31}P NMR spectrum which also exhibited an AB quartet (J 45.8 Hz) although the expected coupling to ^{195}Pt was not reported [35].

When the ligand was changed to the ethylene bridged chelating 'fluorenyl' phosphonium ylide (Fig. 11, $n = 2$), a bis-ylide containing compound was obtained with the structure shown in Fig. 55 [35]. The IR spectrum of this compound exhibited only one Pd–Cl band (352 cm^{-1}) which is virtually identical to that observed for K_2PdCl_4 indicating that the product most likely had a $PdCl_4^-$ anion present. The ^{31}P NMR spectrum exhibited two triplet resonances [35].

2.7. Group 11 metals

The only report of phosphonium cyclopentadienylide complexes of group 11 metals describes the synthesis of the gold

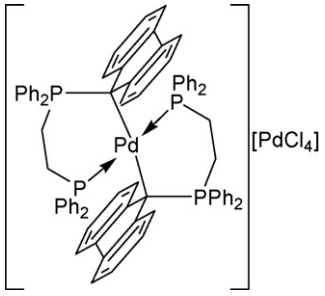

Fig. 55. The palladium complex of the ethylene bridged chelating fluorenyl ylide.

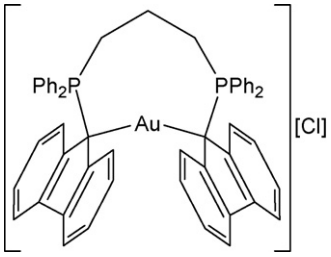

Fig. 56. The proposed structure of the cationic gold chelating bis-ylide complex.

compound of the chelating propylene bridged bis-ylide shown in Fig. 11 [35]. When Me_3PAuCl and this ylide were reacted in a 1:1 ratio, the gold compound shown in Fig. 56 was obtained in 30% yield. No absorption for the Au–Cl stretching mode (usually found between 250 and 400 cm^{-1}) was observed in the IR spectrum, and the ^{31}P NMR spectrum exhibited only a singlet resonance at δ 32.29, consistent with the suggested structure. No ^1H NMR data were provided, but it was reported that conductivity measurements support this assignment although no data for these measurements were provided [35]. In summary, although this structural assignment is plausible, the information provided to substantiate it is incomplete.

2.8. Group 12 metals

As with most of the other transition metal groups, there are few reports of phosphonium cyclopentadienylide complexes of the group 12 metals. In 1976, Holy et al. reported that $C_5H_4PPh_3$ reacts with HgX_2 (X = Cl, Br, I) in THF to form compounds of the type $[(C_5H_4PPh_3)HgX_2]_2$ (Fig. 57) [28,63]. The X-ray structure of the iodido compound was determined, and it was found that the C_5 ring is bound to the mercury atom in an η^1 coordination mode through a σ-bond as in Fig. 57. This was the first report of $C_5H_4PPh_3$ being bound in this way. The P–C_5 bond distance (1.748(7) Å) in this compound is elongated relative to the P–C_5 bond distance in $C_5H_4PPh_3$ (1.718(3) Å) [7,28,63], but the C_5 ring bond distances are only nominally shorter than in the free ligand. The bonding at the β-carbon (see Fig. 57 for labelling) was thought to be a result of steric interactions between the triphenylphosphonium group and the metal halide [28]. The resonances of the α- and β-carbons of the C_5 ring were broadened in the ^{13}C NMR spectra, suggesting the possibility of fluxional behaviour in solution [28]. These compounds represent the potential of phosphonium cyclopentadienylide ligands to provide interesting structures by coordination in different bonding modes. A later report by Roberts detailed similar reactions of $C_5H_4PPh_3$ with mercuric halides followed by quenching

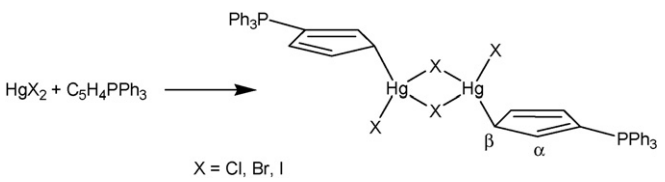

Fig. 57. The synthesis of the η^1-$C_5H_4PPh_3$ mercury halide dimer complex.

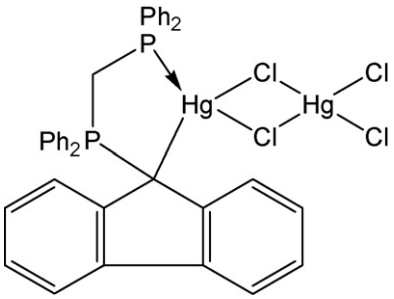

Fig. 58. The proposed structure of the 1:2 mercury complex of the chelating methylene bridged fluorenyl ylide.

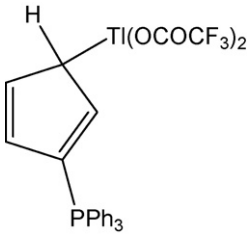

Fig. 59. The thallium complex obtained from the reaction of $C_5H_4PPh_3$ with $Tl(OCOCF_3)_3$.

of the solutions with KBr, but no conclusive spectroscopic or structural information was obtained [29].

The reaction of one equivalent of $HgCl_2$ with two equivalents of the methylene bridged chelating fluorenyl ylide (Fig. 11) was examined by Holy et al. who isolated two products, one soluble in THF, the other not [35]. Elemental analyses suggested that the THF insoluble product had an ylide:$HgCl_2$ ratio of 1:1.5 and that the soluble product had a ratio of 1:2. The ^{31}P NMR spectra of both in DMSO exhibited AB quartets, as expected and consistent with the ^{31}P NMR spectra of the free ligand [49] and of the groups 6 and 10 compounds mentioned above [35]. However, while the values of $J_{P–P}$ of the free ligand and most compounds are in the range 45–70 Hz, that of the soluble product was only 6.0 Hz. The significance of this difference is not clear, but conductivity measurements on this compound indicated that it was non-ionic and a cryoscopic molecular weight determination showed that it was monomeric, and the structure shown in Fig. 58 was suggested. Conductivity measurements showed that the 1:2 compound was not ionic, but low solubility prevented the determination of the compound molecular weight and no structure for this compound was proposed [35].

2.9. Thallium(III) complexes

Roberts reported the reaction of $C_5H_4PPh_3$ and $Tl(OCOCF_3)_3$ in trifluoroacetic acid [29]. It was determined that when $C_5H_4PPh_3$ was dissolved in CF_3CO_2H, a product was obtained with the formula of $C_5H_4PPh_3{\cdot}2CF_3CO_2H$, for which the structure is unknown [29]. After 48 h, a product was obtained which was identified by ^1H NMR spectroscopy to be the structure shown in Fig. 59, similar to the structure shown for a similar mercury compound in Fig. 57 [29]. As with the mercury compounds, fluxional behaviour was possible as peak broadening was observed in the ^1H NMR spectrum.

3. Conclusions

In this review we have discussed all reports concerning the coordination chemistry of phosphonium cyclopentadienylides which we could unearth. It is clear, at this point in time, that very few such ligands have been reported, and thus that there is great scope for the development of new ligands which will make possible exploration of the steric and electronic factors in the coordination chemistry of this class of ligands. In most cases the reports cited have discussed syntheses which entailed substitution of coordinated ligand by one of the phosphonium cyclopentadienylides discussed above. However, we have also pointed out several examples of complexes of phosphonium cyclopentadienylides in which the ylide ligand was generated via indirect methods and was not in fact recognized as such.

We have also cited many instances in the early literature where syntheses of phosphonium cyclopentadienylide complexes were apparently successful but where the products obtained were not characterized satisfactorily by current standards. This situation arose in large part because much of the earlier research on such complexes was carried out before modern NMR and crystallographic methods were available. Interestingly, as we have noted above, the advent of phosphonium cyclopentadienylide coordination chemistry coincided with that of metallocene chemistry and, as is well known, it is metallocene chemistry which has dominated research in organometallic chemistry. It is for this reason that phosphonium cyclopentadienylide coordination chemistry remains largely unexplored.

In view of the importance of definitive ^1H and ^{31}P NMR spectroscopy and X-ray crystallography in the field of phosphonium cyclopentadienylide coordination chemistry, we have throughout this review drawn the reader's attention to situations where the requisite data are lacking as well as to those compounds for which the data are available and are useful for deducing structures. To facilitate comparisons, we also present all ^1H and ^{31}P NMR data which are available in Table 1 and all relevant C_5H_4 ring bond length data which are available in Table 2. Both tables utilize the atom numbering for the carbon and hydrogen atoms of the C_5H_4 rings shown in Fig. 60.

Few trends in chemical shifts are obvious in Table 1, although coordination of $C_5H_4PPh_3$ and $C_5H_4PMePh_2$ does generally result in shielding of the C_5H_4 ring protons resonances relative to the free ligands. The extent of the shielding apparently correlates in many cases with the oxidation state of the metal, with metals in higher oxidation states resulting in less shielding. The bond length data in Table 2 show that the P–C_5 (P–C(1) of Fig. 60) distances in coordinated phosphonium cyclopentadienylides are invariably longer than those of the free ligands,

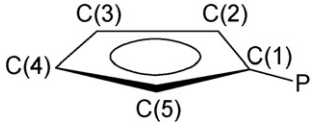

Fig. 60. Labelling scheme utilized in Tables 1 and 2 to facilitate comparisons of the NMR and crystallographic data.

suggesting increased importance of the zwitterionic structures such as those of Figs. 1 and 5 in the coordination compounds. This result is as expected if the ring is behaving as an aromatic, six-electron donor isoelectronic with, e.g. benzene and the cyclopentadienyl ligand. Consistent with this interpretation, the C–C bond lengths of the C_5 rings are generally comparable with those of benzene although a degree of alternation is apparent. Thus the C(2)–C(3)/C(4)–C(5) bonds are usually shorter than the others, suggesting that the "diene" structures of Figs. 1 and 5 are not irrelevant in the coordination compounds although the extent of alternation appears to decrease on coordination.

References

[1] F. Ramirez, S. Levy, J. Org. Chem. 21 (1956) 488.
[2] F. Ramirez, S. Levy, J. Org. Chem. 21 (1956) 1333.
[3] F. Ramirez, S. Levy, J. Am. Chem. Soc. 79 (1957) 67.
[4] F. Ramirez, S. Dershowitz, J. Org. Chem. 22 (1957) 41.
[5] F. Ramirez, S. Levy, J. Am. Chem. Soc. 79 (1957) 6167.
[6] F. Ramirez, S. Levy, J. Org. Chem. 23 (1958) 2035.
[7] H.L. Ammon, G.L. Wheeler, P.H. Watts, J. Am. Chem. Soc. 95 (1973) 6158.
[8] G.A. Gray, J. Am. Chem. Soc. 95 (1973) 5092.
[9] E.W. Abel, A. Singh, G. Wilkinson, Chem. Ind. (London) (1959) 1067.
[10] J.C. Kotz, D.G. Pedrotty, J. Organomet. Chem. 22 (1970) 425.
[11] D. Cashman, F.J. Lalor, J. Organomet. Chem. 32 (1971) 351.
[12] D. Cashman, F.J. Lalor, J. Organomet. Chem. 24 (1970) C29.
[13] V.I. Zdanovitch, A.I. Yurtanov, A.Z. Zhakaeva, V.N. Setkina, D.N. Kursanov, Izv Akad Nauk SSR Ser. Khim. 6 (1973) 1375.
[14] V.N. Setkina, A.Z. Zhakaeva, G.A. Panosyan, V.I. Zdanovitch, P.V. Petrovskii, D.N. Kursanov, J. Organomet. Chem. 129 (1977) 361.
[15] T. Debaerdemaeker, Z. Kristallogr. 153 (1980) 221.
[16] A.N. Nesmeyanov, N.E. Kolobova, V.I. Zdanovitch, A.Z. Zhakaeva, J. Organomet. Chem. 107 (1976) 319.
[17] V.I. Zdanovitch, N.E. Kolobova, N.I. Vasyukova, Y.S. Nekrasov, G.A. Panosyan, P.V. Petrovskii, A.Z. Zhakaeva, J. Organomet. Chem. 148 (1978) 63.
[18] N.L. Holy, N.C. Baenziger, R.M. Flynn, Angew. Chem. Int. Ed. Engl. 17 (1978) 686.
[19] N.C. Baenziger, R.M. Flynn, N.L. Holy, Acta Crystallogr. B B35 (1979) 741.
[20] A.J. Blake, B.F.G. Johnson, S. Parsons, D.S. Shephard, J. Chem. Soc. Dalton Trans. (1995) 495.
[21] G. Tresoldi, A. Recca, P. Finocchiaro, F. Faraone, Inorg. Chem. 20 (1981) 3103.
[22] G. Tresoldi, F. Faraone, P. Piraino, F.A. Bottino, J. Organomet. Chem. 231 (1982) 265.
[23] B.L. Booth, K.G. Smith, J. Organomet. Chem. 220 (1981) 229.
[24] C.G. Pierpont, H.H. Downs, K. Itoh, H. Nishiyama, Y. Ishii, J. Organomet. Chem. 124 (1976) 93.
[25] M.-F. Hirai, M. Miyasaka, K. Itoh, Y. Ishii, J. Chem. Soc. Dalton Trans. (1979) 1200.
[26] M.-F. Hirai, M. Miyasaka, K. Itoh, Y.Y Ishii, J. Organomet. Chem. 165 (1979) 391.
[27] G. Bombieri, G. Tresoldi, F. Faraone, G. Bruno, P. Cavoli-Belluco, Inorg. Chim. Acta 57 (1982) 1.
[28] N.L. Holy, Baenziger, R.M. Flynn, D.C. Swenson, J. Am. Chem. Soc. 98 (1976) 7823.
[29] R.M.G. Roberts, Tetrahedron 36 (1980) 3295.
[30] N.L. Holy, T.E. Nalesnik, L.T. Warfield, Inorg. Nucl. Chem. Lett. 13 (1977) 569.
[31] T. Nalesnik, L. Warfield, N. Holy, J. Layton, S. Smith, Inorg. Nucl. Chem. Lett. 13 (1977) 523.
[32] N.L. Holy, T. Nalesnik, L. Warfield, M. Mojesky, J. Coord. Chem. 12 (1983) 157.
[33] G. Vettese, M.C. Baird, Unpublished results.
[34] K. Iwata, S. Yoneda, Z. Yoshida, J. Am. Chem. Soc. 93 (1971) 6745.
[35] N. Holy, U. Deschler, H. Schmidbaur, Chem. Ber. 115 (1982) 1379.
[36] F. Mathey, J.-P. Lampin, Tetrahedron 31 (1975) 2685.
[37] J.H. Brownie, H. Schmider, M.C. Baird, Organometallics 26 (2007) 1433.
[38] J.H. Brownie, H. Schmider, M.C. Baird, D.R. Laws, W.E. Geiger, Organometallics 26 (2007) 5890.
[39] C.P. Casey, R.M. Bullock, W.C. Fultz, A.L. Rheingold, Organometallics 1 (1982) 1591.
[40] B.H. Freeman, D. Lloyd, M.I.C. Singer, Tetrahedron 28 (1972) 343.
[41] D. Lloyd, M.I.C. Singer, J. Chem. Soc. C (1971) 2941.
[42] F. Ramirez, S. Levy, J. Org. Chem. 23 (1958) 2036.
[43] B.H. Freeman, D. Lloyd, Tetrahedron 30 (1974) 2257.
[44] B.H. Freeman, D. Lloyd, M.I.C. Singer, Tetrahedron 30 (1974) 211.
[45] P.C. Crofts, M.P. Williamson, J. Chem. Soc. C (1967) 1093.
[46] K.A. Rufanov, B. Ziemer, M. Hummert, S. Schutte, Eur. J. Inorg. Chem. (2004) 4759.
[47] L.A. Pinck, G.E. Hilbert, J. Am. Chem. Soc. 69 (1947) 723.
[48] A.W. Johnson, S.Y. Lee, R.A. Swor, L.D. Royer, J. Am. Chem. Soc. 88 (1966) 1953.
[49] H. Schmidbaur, U. Deschler, Chem. Ber. 114 (1981) 2491.
[50] J.H. Shin, B.M. Bridgewater, G. Parkin, Organometallics 19 (2000)5155.
[51] J.C. Kotz, C.D. Turnipseed, J. Chem. Soc. Chem. Commun. (1970) 41.
[52] H. Alper, R.A. Partis, J. Organomet. Chem. 44 (1972) 371.
[53] G.P. Sollott, H.E. Mertwoy, S. Portnoy, J.L. Snead, J. Org. Chem. 28 (1963) 1090.
[54] W.E. McEwen, J.E. Fountaine, D.N. Schulz, W.-I. Shaiu, J. Org. Chem. 41 (1976) 1684.
[55] W.E. McEwen, C.E. Sullivan, R.O. Day, Organometallics 2 (1983) 420.
[56] C. Imrie, T.A. Modro, P.H. Van Rooyen, Polyhedron 13 (1994) 1677.
[57] K. Kirchner, K. Mereiter, R. Schmid, H. Taube, Inorg. Chem. 32 (1993) 5553.
[58] W. Watanabe, M. Sato, T. Takayama, Organometallics 18 (1999) 5201.
[59] A.J. Deeming, N.I. Powell, C. Whittaker, J. Chem. Soc. Dalton Trans. (1991) 1875.
[60] R.J. McKinney, Inorg. Chem. 21 (1982) 2051.
[61] M.E. Rerek, F. Basolo, J. Am. Chem. Soc. 106 (1984) 5908.
[62] K. Abdulla, B.L. Booth, C. Stacey, J. Organomet. Chem. 293 (1985) 103.
[63] N.C. Baenziger, R.M. Flynn, C.C. Swenson, N.L. Holy, Acta Crystallogr. B 34 (1978) 2300.