Journal of Organometallic Chemistry 557 (1998) 37–68

Functionalized ylides: new trends in organometallic chemistry[1]

Umberto Belluco [a], Rino A. Michelin [a,*], Mirto Mozzon [a], Roberta Bertani [b], Giacomo Facchin [b], Livio Zanotto [b], Luciano Pandolfo [c]

[a] *Dipartimento di Processi Chimici dell'Ingegneria, Università di Padova, Via Marzolo 9, 35131 Padova, Italy*
[b] *Centro Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione, C.N.R., Via Marzolo 9, 35131 Padova, Italy*
[c] *Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Via Marzolo 1, 35131 Padova, Italy*

Received 29 July 1997

Abstract

The coordination and organometallic chemistry of P- and As-carbonyl stabilized ylides is reviewed. As a general feature, the coordination chemistry of $R_3ECHCOR'$-type ($E = P$, As) ligands appears to be dominated by C(ylide) metal coordination, although a few examples of O(ylide)-bound complexes are known. The factors addressing C(ylide)-*vs.* O(ylide)-coordination in Pt(II) and Pd(II) systems are examined. The Ni(II) complexes containing P,O-chelate ylide ligands are also discussed, with a special emphasis on their catalytic activity. The synthesis and reactivity of phosphonium functionalized isocyanides and their corresponding ylides, which provide a new route to metal coordinated indole systems, are described. Finally, the reactivity of $Ph_3PC{=}C{=}O$ towards metal substrates is summarized including the formation of ketenyl complexes. © 1998 Elsevier Science S.A.

Keywords: Ylides; Ligand; Indole systems; Ketenyl

1. Introduction

P- and As-ylides are remarkable ligands which have attracted much attention in synthetic, catalytic and theoretical fields of transition metal chemistry [1]. The large number of reports on the organometallic ylide chemistry covering most of the d-block and some of the f-block elements may be explained with the structural variety of the ylide coordination modes [1]. The coordination chemistry of ylides has been previously reviewed by Schmidbaur [2] and Kaska [3], who described the synthesis of metal–ylide complexes from 'preformed' ylides or through various reactions involving metal complexes containing suitable C_1-substrates and phosphines.

Within this research area, ylides containing a second functional group have become increasingly interesting since they can provide new synthetic and catalytic routes in organometallic chemistry.

Herein we wish to describe the reaction chemistry of three functionalized ylide systems:

1. carbonyl stabilized ylides;
2. phosphonium functionalized isocyanides and their corresponding ylides;
3. the cumulenic ylide, ketenylidenetriphenylphosphorane, Ph_3PCCO.

2. Carbonyl stabilized ylides

Carbonyl stabilized ylides of the type $R_3E = C(R')COR''$ ($E = P$, As; R, R′, $R'' = H$, alkyl or aryl groups) exhibit interesting properties such as a high stability (they can be handled in air) and an ambidentate character as ligands

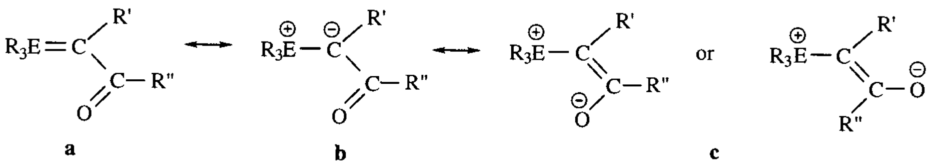
---

* Corresponding author. Tel.: + 39 49 8275522; fax: + 39 49 8275525; e-mail: michelin@ux1.unipd.it

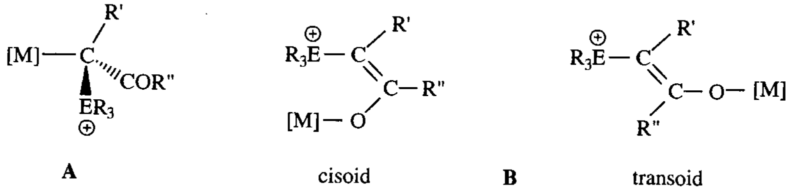
[1] Dedicated to Professor Robert J. Angeliei on the occasion of his 60th birthday.

PII S0022-328X(97)00733-X

that can be rationalized in terms of the resonance forms *a–c* (where *c* is represented by the *cis* and *trans* geometrical isomers).



Forms *b* and *c* account for the metal C-coordination **A** and O-coordination **B** (either in the *cisoid* and *transoid* forms), respectively:



The chemical behaviour of carbonyl-stabilized ylides is largely dominated by the C(ylide)-coordination [1,4], while very few examples of O-coordinated ylides are known [5].

2.1. Metal–C(ylide) coordination

Most of the reactions of transition metal complexes with carbonyl-stabilized ylides were initially investigated using Pd(II) and Pt(II) as metal centers. The first report described the synthesis of a series of bis(ylide) complexes obtained by reaction of BPPY with $PdCl_2$ and $PtCl_2$ [6] (Scheme 1). The C(ylide)-coordination in all of these complexes was proposed on the basis of spectroscopic data. The infrared spectra in the solid state show ν(C=O) in the range 1627–1672 cm^{-1}, at higher wavenumbers with respect to the free ylide (BPPY, ν(C=O) 1513 cm^{-1}). In the ^1H NMR spectra, the CH ylide proton is shifted downfield compared to that of the free ylide (BPPY, 4.41 ppm) as a consequence of the inductive effect of the metal center. Furthermore, the values of the $^2J_{HP}$ coupling constants between the methine proton and the phosphorus atom of the ylide ligands are lower (ca. 5 Hz) than those of the free ylide (BPPY, 23.2 Hz) in agreement with a $sp^2 \rightarrow sp^3$ rehybridization of the ylide carbon upon coordination to the metal atom. The $^{13}C\{^1H\}$ NMR spectra show the ylidic carbon atom shifted upfield (<40 ppm) with respect to the free ylide (BPPY, 50.4 ppm), while the adjacent carbonyl carbon (BPPY, 184.9 ppm) is strongly shifted downfield (>200 ppm).

Bravo et al. [7] reported a detailed study of the ^{13}C NMR spectra of some phosphonium, arsonium, sulfonium and pyridinium keto-stabilized salts and their corresponding ylides and also of their Pd(II) complexes. The spectroscopic data ($^1J_{CH}$, $\delta_{C(ylide)}$, $\delta_{(CO)}$) found for the ylides of phosphorus, arsenic and sulfur were consistent with a sp^2-hybridized ylidic carbon atom with a strong, localized negative charge, while for the pyridinium ylides, this charge is much more delocalized on the pyridine moiety. They observed [7] that the coordination generally occurs selectively through the C-ylide atom and the Pd–C(ylide) bond is strongly polarized with a high electron density on the C(ylide) atom, which in this case cannot be delocalized through the resonance forms *a–c* as in the free ligands.

The keto-stabilized P- and As-ylides of the type $R_3P{=}CHCOR$ (R = Me, Ph), $Ph_3As{=}CHCOR$, and pyridinium ylides ($C_5H_5\overset{+}{N}{-}\overset{-}{C}HCOR$) were shown to displace weakly coordinated ligands (styrene or benzonitrile) on Pd(II)

$$[MX_2] \xrightarrow{Ph_3P=CHR'} [X_2M(Ph_3PCHR')_2]$$

1

M = Pd, Pt; X = Cl; R' = COPh[6a]

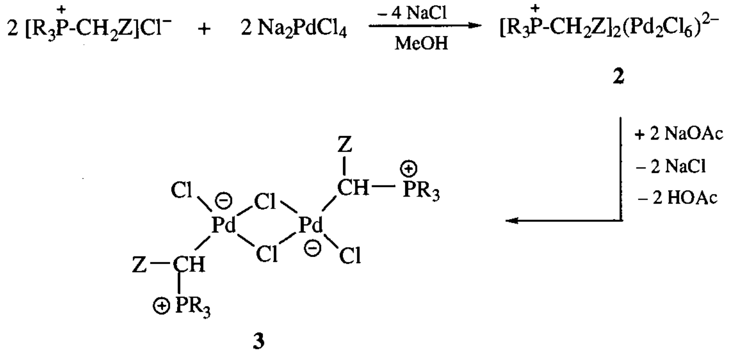
M = Pd; X = Cl; R' = COPh, COMe, COOMe[7]

M = Pd, Pt; X = Cl, SCN; R' = COPh, COMe, COOMe, COOEt, COCN[8]

Scheme 1.

compounds to form complexes of the general formula $[PdCl_2(ylide)_2]$ [8,9] which exhibit a *trans* square planar geometry in the solid state, while they are present as a mixture of the *trans* and *cis* isomers in solution.

An alternative method to the synthesis of palladium(**II**) complexes of stabilized phosphonium ylides bearing electron-withdrawing substituents (e.g. acyl, ethoxycarbonyl, carbonyl and cyano groups) involves the initial reaction of the phosphonium salt with sodium palladate to give the bis(phosphonium)hexachlorodipalladate complexes **2**, which upon reaction with sodium acetate, afford the final chloro-bridged dinuclear products **3** (Eq. 1) [10].



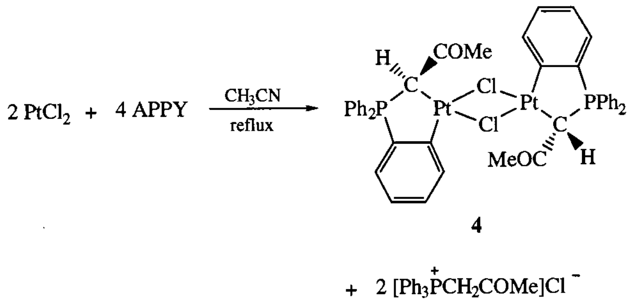
$$2\,[R_3\overset{+}{P}\text{-}CH_2Z]Cl^- + 2\,Na_2PdCl_4 \xrightarrow[MeOH]{-4\,NaCl} [R_3\overset{+}{P}\text{-}CH_2Z]_2(Pd_2Cl_6)^{2-} \quad (1)$$

2

3

$PR_3 = PPhMe_2$; $Z = COPh$
$PR_3 = PPh_3$; $Z = COMe, COOEt, CONH_2, CN$

Burmeister et al. [11] reported that in some reactions of the metal dichlorides $[MCl_2]$ ($M = Pd, Pt$) with carbonyl stabilized ylides in a 1:2 molar ratio carried out in refluxing CH_3CN for 4 h, orthometalated complexes of the type **4** and onium salts were obtained. One of these complexes e.g. $[Pt(\mu\text{-}Cl)\{CH_3C(O)CHP(C_6H_4)(C_6H_5)_2\}]_2$ (**4**) was structurally characterized (Eq. 2).



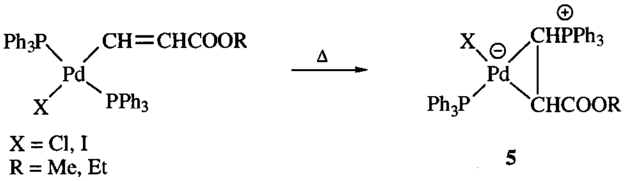
$$2\,PtCl_2 + 4\,APPY \xrightarrow[reflux]{CH_3CN} \mathbf{4} + 2\,[Ph_3\overset{+}{P}CH_2COMe]Cl^- \quad (2)$$

4

Conversely, an analogous reaction of $[PdCl_2]$ with BBuPY [12] in refluxing CH_3CN gives the dinuclear complex $[PdCl(\mu\text{-}Cl)\{CH(P\text{-}n\text{-}Bu_3)COPh\}]_2$, where the ylide is coordinated only through the ylide–methine carbon, as shown by an X-ray structural analysis.

Vicente et al. in a reinvestigation of the reactivity of CMPPY with $[PdCl_2]$ [13] found that the reactions performed at room temperature, gave in high yield, after stirring for 15 min, the bis(ylide) complex $[PdCl_2\{CH(PPh_3)CO_2Me\}_2]$. On the other hand, when the ylide was added to a refluxing solution of $[PdCl_2]$ in acetonitrile, the metalated complex $[Pd\{CH\{P(2\text{-}C_6H_4)Ph_2\}(CO_2Me)\}(\mu\text{-}Cl)]_2$ was obtained, as previously reported by Burmeister [11].

Metalate derivatives were also obtained by heating in benzene vinylpalladium complexes of the type $[Pd(\eta^1\text{-}CH{=}CHCOOR)(X)(PPh_3)_2]$, according to Eq. 3 [14], where η^2-olefin-ylide palladium complexes of type **5** were formed:



5

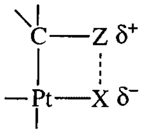
(3)

The chloro-bridge splitting by keto-stabilized ylides has been reported to yield complexes of the type $[MCl_2L(CHCOPhZ)]$,(**6**), according to Eq. 4 [15]:

$$1/2[MCl(\mu\text{-}Cl)(PMe_2Ph)]_2 \xrightarrow{ZCHCOPh} \underset{\mathbf{6}}{[MCl_2(PMe_2Ph_2)(CHCOPhZ)]} \qquad (4)$$

M = Pd, Pt; Z = p-$CH_3C_5H_4N$; $CH_3(C_6H_5)_2P$; $(C_6H_5)_3As$; $(CH_3)_2S$

Also in this case, the ylides coordinate to palladium and platinum centers through the methinic carbon, as indicated by IR ($\nu_{(CO)}$ at higher wavenumbers with respect to the corresponding free ylides) and ^1H NMR data (observation of spin–spin coupling between the ylide methine proton and the ^{195}Pt nucleus). Furthermore, it was observed that the values of the coupling constant between the ^{195}Pt nucleus and the ylide methine proton, $^2J_{PtCH}$, in *trans*-$[PtCl_2LY]$ complexes (L = $PPhMe_2$, PMe_3; Y = ZCHCOPh) increase with increasing basicity of the ylide according to the following order: p-$CH_3C_5N_4NCHCOPh > (C_6H_5)_3AsCHCOPh > (CH_3)_2SCHCOPh > CH_3(C_6H_5)_2PCHCOPh$. In *trans*-$[PtX_2(PPhMe_2)Y]$ (X = Cl, Br, I; Y = p-$CH_3C_5H_4NCHCOPh$, $(CH_3)_2SCHCOPh$, $CH_3(C_6H_5)_2PCHCOPh$) complexes, the $^2J_{PtCH}$ values increase and ν(Pt–C) move to higher wavenumbers in the order Cl < Br < I, probably due to an interaction of the positively charged ylide heteroatom with the halogen of the type **C**.

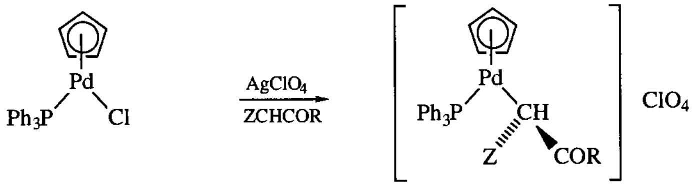


Z = heteroatom group

C

This interaction polarizes the platinum–halogen bond decreasing the *s* character and resulting in an increase in the electron density in the 6*s* valence orbital at the platinum atom. A similar effect may occur in the ylide carbon–heteroatom bond. The combined polarizations would eventually cause a high-frequency shift of ν(Pt–C) and an increase of $^2J_{PtCH}$.

The cyclopentadienyl-ylide Pd(II) complexes of the type $[Pd(\eta^5\text{-}C_5H_5)(PPh_3)(Y)][ClO_4]$ (Y = APPY, BPPY, BDMSY) have been prepared according to Eq. 5 [16]:

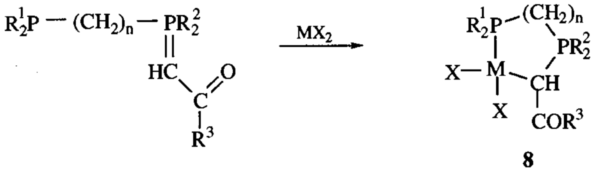


(5)

Z = PPh_3; R = CH_3, Ph
Z = Me_2S; R = Ph

7

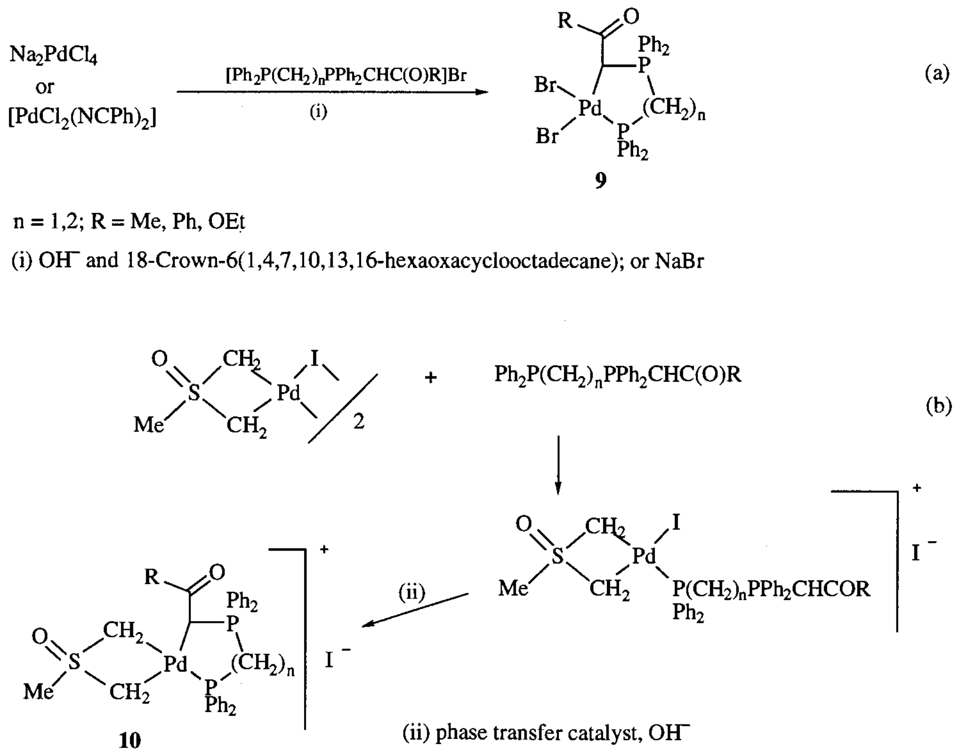
Ylides with a terminal phosphane functionality on the side alkyl chain were found to be good chelating agents towards Pd(II) and Pt(II) halides; the formation and structure of the reaction products have been studied in detail [17] (Eq. 6).



8

(6)

n = 1; M = Pd, Pt; X = Cl; $R^1 = R^2 = R^3$ = Ph; $R^1 = R^2$ = Ph; R^3 = Me, OMe
n = 1; M = Pd, Pt; X = Cl, Br, I, SCN; $R^1 = R^2$ = Ph; R^3 = Ph, Me, OMe, OEt
n = 0; M = Pd, Pt; X = Cl; $R^1 = R^2$ = Ph; R^3 = Ph, Me, OMe
n = 1; M = Pd, Pt; X = Cl; $R^1 = R^2$ = CH_2Ph; R^3 = Ph
n = 2; M = Pd, Pt; X = Cl; $R^1 = R^2$ = Ph; R^3 = Ph, Me, OMe



n = 1,2; R = Me, Ph, OEt

(i) OH^- and 18-Crown-6(1,4,7,10,13,16-hexaoxacyclooctadecane); or NaBr

(ii) phase transfer catalyst, OH^-

Scheme 2.

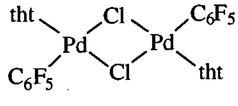
The X-ray structural determination of one of the above mentioned complexes, e.g. $[PdCl_2\{Ph_2PCH_2CH_2PPh_2CHC(O)Ph\}]$ [17](d) confirms that the ylide ligand coordinates to palladium through the ylide carbon atom (Pd–C = 2.115(15) Å) and the phosphine phosphorus (Pd–P = 2.230(8) Å) forming a six-membered chelate ring.

Related chelate ylide complexes have been obtained by Lin et al. (using phase-transfer technique) [18] who prepared phosphorus ylide complexes of the type $[PdBr_2Ph_2P(CH_2)_nPPh_2CHC(O)R\}]$ ($n = 1$ or 2; R = Me, Ph or OEt) (Scheme 2(a)) and mixed sulphur and phosphorus ylide complexes of the type $[Pd\{(CH_2)_2S(O)Me\}\{Ph_2P(CH_2)_nPPh_2CHC(O)R\}][I]$ according to Scheme 2(b). The mixed ylide complex $[Pd\{(CH_2)_2S(O)Me\}\{Ph_2PCH_2PPh_2CHC(O)Ph\}][I]$ CH_2Cl_2 H_2O has also been investigated by X-ray crystallography. The Pd–C bond length of 2.183(5) Å of the phosphorus ylide moiety was found to be longer than that observed for the sulphur ylide ligand [2.094(3) Å (average)].

The formation of Pd(II) complexes containing keto-stabilized ylides of the type $Ph_2P(CH_2)_nPPh_2CHCOR$ ($n = 1$, $R = CH_3$, C_6H_5; $n = 2$, $R = C_6H_5$) acting as monodentate P-donor or bidentate chelating P,C-donor ligands was also reported by Uson et al. [19]. The reaction of the ylides $Ph_2PCH_2PPh_2CHCOPh$ and $Ph_2P(CH_2)_nPPh_2CHCOMe$ with a dichloromethane solution of *trans*-$[Pd(C_6F_5)_2(tht)_2]$ (tht = tetrahydrothiophene) gave the displacement of the tht ligands to form bis-C(ylide) metal complexes (Eq. 7):

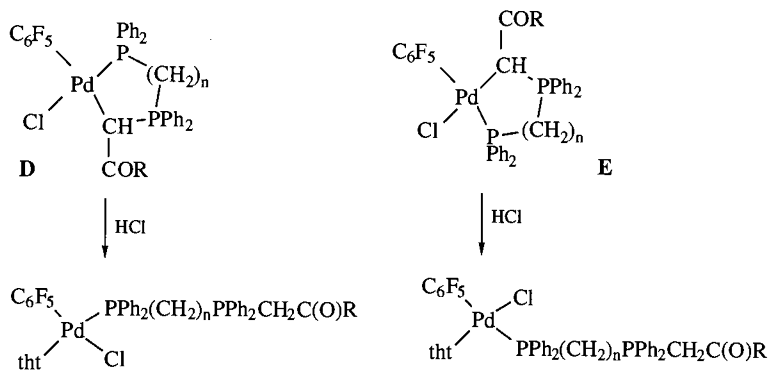
$$\textit{trans}\text{-}[Pd(C_6F_5)_2(tht)_2] + 2\text{ ylide} \longrightarrow 2\text{ tht} + \underset{\mathbf{11}}{\textit{trans}\text{-}[Pd(C_6F_5)_2(ylide)_2]} \qquad (7)$$

Conversely, complexes of the type $[PdCl(C_6F_5)(ylide)]$ were obtained by the addition of the same type of ylides, e.g. $Ph_2P(CH_2)_nPPh_2CHCOR$, to a benzene solution of the neutral dinuclear Pd(II) complex $[Pd(\mu\text{-}Cl)(C_6F_5)(tht)]_2$ [19] (Eq. 8):



$$+ \; 2\text{ ylide} \longrightarrow 2\,\underset{\mathbf{12}}{[PdCl(C_6F_5)(ylide)]} \qquad (8)$$

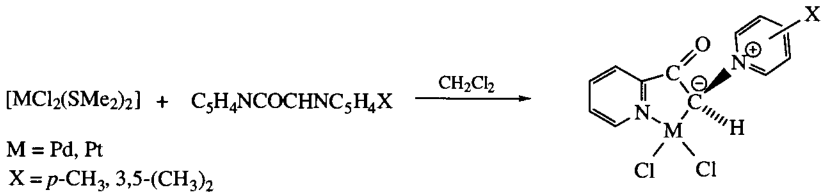
ylide = $Ph_2P(CH_2)_nPPh_2CHCOR$ (R = Ph, n = 1, 2; R = Me, n = 1)



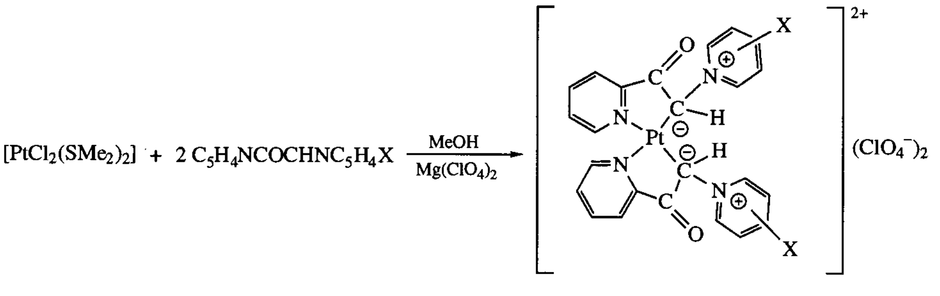
Scheme 3.

The ligands chelate the Pd(II) metal center through the C(ylide) atom and the terminal P-atom of the phosphine. ^{31}P NMR data of the complexes indicate that in solution both **D** and **E** isomers are present (Scheme 3). Reaction with HCl gave C(ylide)-protonation with formation of complexes having only the P-phosphine atom coordinated to the Pd(II) center (Scheme 3).

The ylide ligands 2-pyridylcarbonylmethylides, $C_5H_4NC(O)CHZ$ (Z = 4-picoline, 3,5-lutidine), were found to chelate Pd(II) and Pt(II) via the ylide carbon and pyridine nitrogen atoms [20] as shown in Eq. 9:



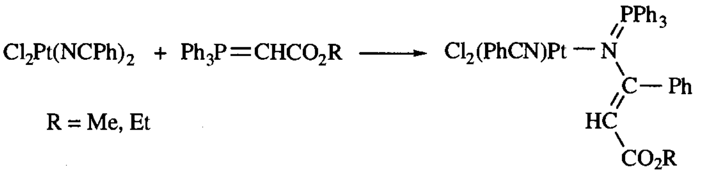
13



14

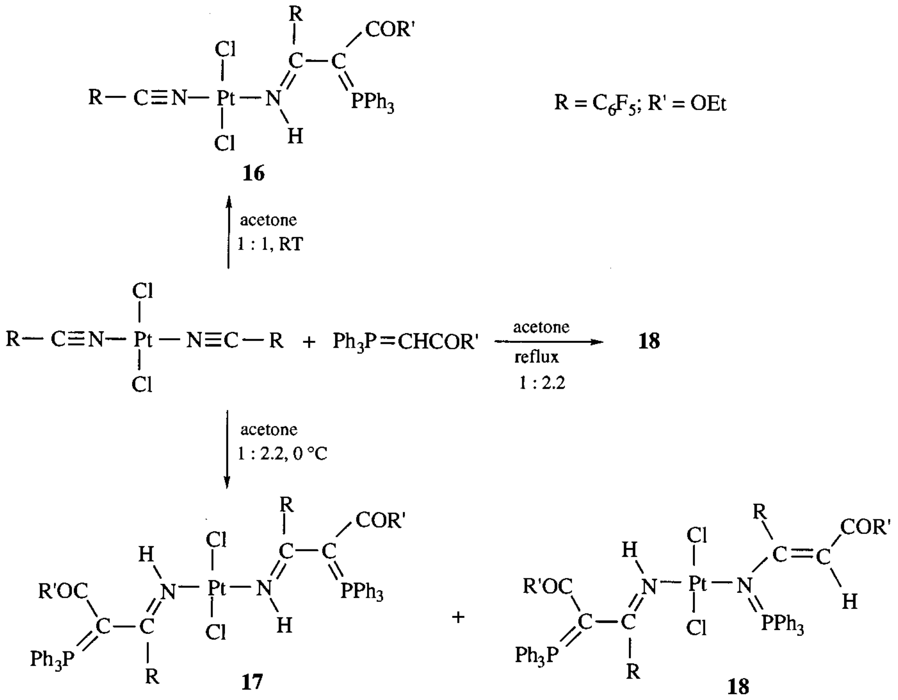
(9)

The ylides $Ph_3P{=}CHCO_2R$ (R = Et,Me) were reported to add to a benzonitrile ligand in *trans*-$[PtCl_2(NCPh)_2]$ to give iminophosphorane complexes of the type $[PtCl_2\{E\text{-}N({=}PPh_3)C(Ph){=}CHCO_2R\}(NCPh)]$ through a process which has been suggested to involve C–P(ylide) bond cleavage and C=C bond formation [21]. The complex with R = Et has been characterized also by an X-ray structural determination. The reaction proceeds through an initial nucleophilic attack of the ylide carbon on the coordinated nitrile carbon [22], followed by migration of the PPh_3 group to the imino nitrogen (Eq. 10).



15

(10)

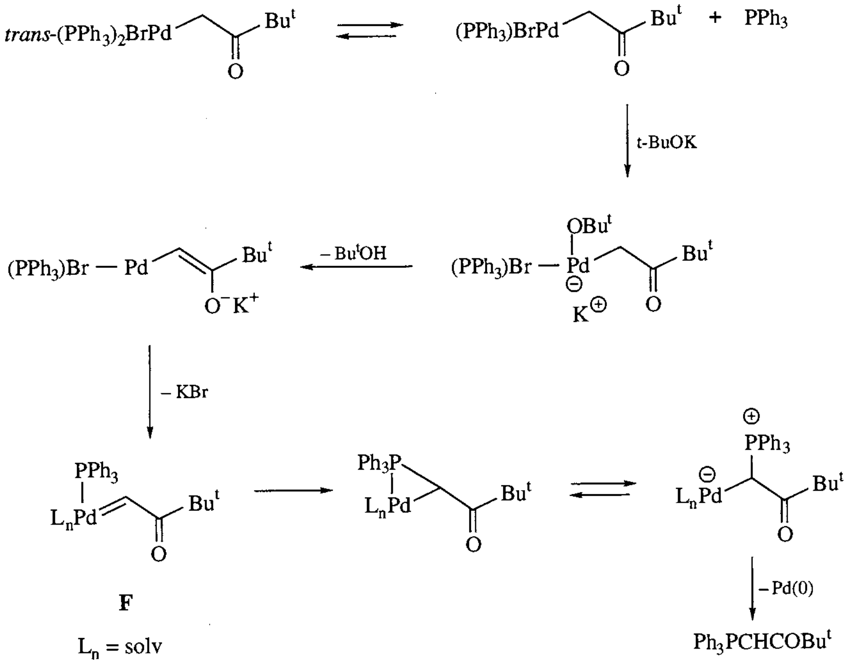


Scheme 4.

It is noteworthy that iminophosphorane complexes are generally prepared using $R_3P{=}NR'$ ligands, although some Ni(II) complexes and one Ir(I) complex were obtained by reacting nitrosyl derivatives with PPh_3 [23](a) and by an intramolecular attack of a coordinated PPh_3 molecule on an imino nitrogen atom [23](b), respectively.

Similar reactions of the pentafluorobenzonitrile ligands with $Ph_3P{=}CHCO_2Et$ gave different products depending on the reaction conditions [24] (Scheme 4). When an equimolecular mixture of $[PtCl_2(NCC_6F_5)_2]$ and the ylide was stirred in acetone for 24 h at room temperature, the complex containing one *N*-bonded *β*-iminophosphorus ylide ligand *trans*-$[PtCl_2\{NH{=}C(C_6F_5)C({=}PPh_3)CO_2Et\}\{NCC_6F_5\}$,(**16**), was obtained in high yield. On the other hand, when $[PtCl_2(NCC_6F_5)_2]$ and $Ph_3P{=}CHCO_2Et$ (1:2.2 molar ratio) were stirred in acetone at 0°C for 30 min, a mixture containing *trans*-$[PtCl_2\{NH{=}C(C_6F_5)C({=}PPh_3)CO_2Et\}_2]$ (**17**), and *trans*-$[PtCl_2\{E\text{-}N({=}PPh_3)C(C_6F_5){=}CHCO_2Et\}\{E\text{-}NH{=}C\text{–}(C_6F_5)C({=}PPh_3)CO_2Et\}]$ (**18**), in a 2:3 molar ratio was formed. This latter complex was the only reaction product obtained by refluxing in acetone for 2 h the initial nitrile complex and the ylide in a 1:2.2 molar ratio.

These results were rationalized by assuming that complexes **16** and **17** were formed by addition of the ylide to the nitrile carbon with subsequent migration of the ylidic hydrogen to the imino nitrogen, while the formation of complex **18** involved the migration of the PPh_3 group as prevoiusly observed [22]. The selective formation of the *E*-isomer (H and R in *trans* position) suggests that the attack of the ylide occurs *trans* to the more hindered group (i.e. the platinum center).

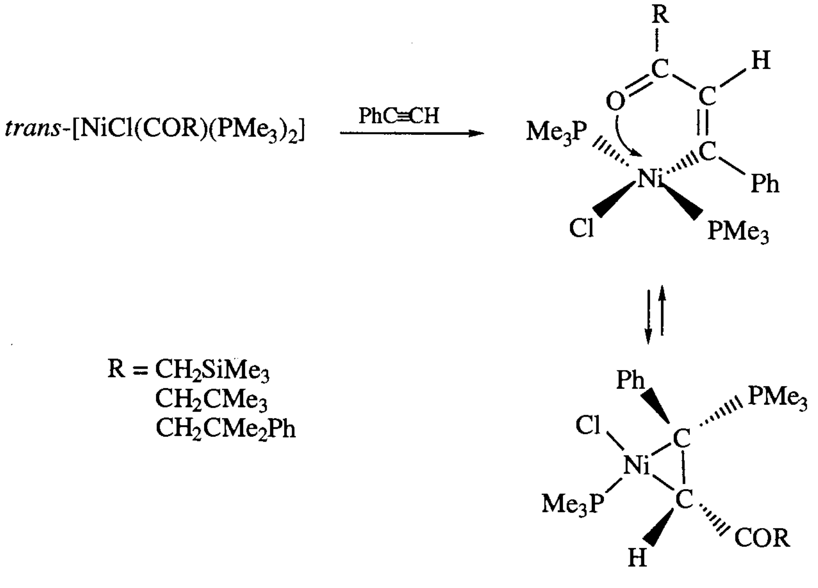


Scheme 5.

$Ph_3P{=}CHCOBu^t$ was reported to be formed in good yield by treatment of $[Pd\{CH_2C(O)Bu^t\}Br(PPh_3)_2]$ with t-BuOK in THF at −63°C. The reaction proceeds through a low-valent palladium alkylidene intermediate **F**, which then rearranges to a phosphacyclopropane species (that can be seen as a resonance structure of a coordinated ylide) [25] according to the proposed reaction mechanism (Scheme 5).

As for metals different from palladium and platinum, the formation of a nickelacyclopropane complex $[\overline{Ni\{C(Ph)(PMe_3)C}(H)(COCH_3CMe_2Ph)\}Cl(PMe_3)_2]$ (19), formally an ylide both coordinated through the ylidic carbon and a second carbon atom, has been reported according to Eq. 11 [26].

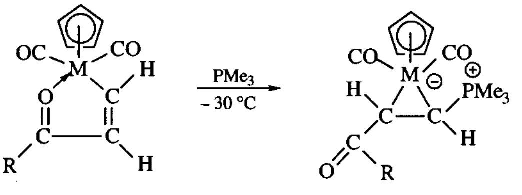
The reaction proceeds by insertion of PhC≡CH into the Ni–COR bond of the corresponding $[NiCl(COR)(PMe_3)_2]$ derivatives to form intermediates of the type $[Ni\{C(Ph){=}C(H)CO(CH_2R)\}Cl(PMe_3)_2]$. These latter reversibly rearrange in solution to yield the nickelacyclopropane complexes $[\overline{Ni\{C(Ph)(PMe_3)C}(H)(COCH_2R))\}Cl(PMe_3)_2]$ one of which, R = CMe_2Ph, was characterized by X-ray analysis [26].



(11)

19

Related metallacyclopropane derivatives [27] were reported to be formed by addition of PMe_3 to five-membered metallacyclic vinylketone complexes of the type $[Cp\overline{M(CO)_2(HC{=}CH{-}CO}R)]$ (M = Mo, W) (Eq. 12):



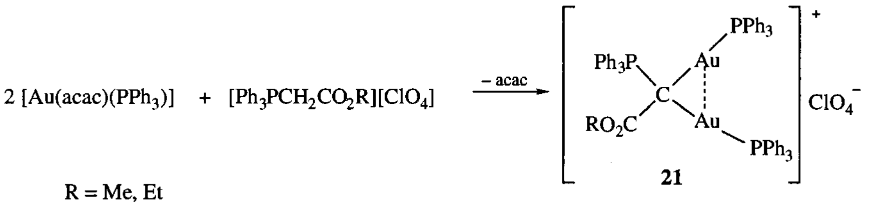
20

M = Mo, W; R = Me, Et, n–Bu

(12)

The reactivity of the ylide $Ph_3P{=}CHC(O)NMe_2$ with [AuCl(tht)] has been extensively studied [28]. The reaction carried out in a 1:1 molar ratio in dichloromethane yields quantitatively $[AuCl\{CH(PPh_3)C(O)NMe_2\}]$, which reacts with Cl_2 to afford $[AuCl_3\{CH(PPh_3)C(O)NMe_2\}]$ or with another equivalent of the ylide and $NaClO_4$ to form $[Au\{CH(PPh_3)C(O)NMe_2\}_2][ClO_4]$ [28](a). The analogous silver complex $[Ag\{CH(PPh_3)C(O)NMe_2\}_2][ClO_4]$ has been also reported [28](c). The phosphonium salt $[Ph_3PCH_2C(O)NMe_2][ClO_4]$ reacts with $[Au(acac)(PPh_3)]$ (acac = acetylacetonate) to afford $[Au\{CH(PPh_3)C(O)NMe_2\}(PPh_3)][ClO_4]$ or $[(AuPPh_3)_2\{\mu\text{-}C(PPh_3)C(O)NMe_2\}][ClO_4]$ depending on the reaction conditions.

The structure of $[\{Au(PPh_3)\}_2\{\mu\text{-}C(PPh_3)C(O)NMe_2\}][ClO_4]$ was confirmed by an X-ray diffraction study [28](a). The related dinuclear complex $[\{Au(PPh_3)\}_2\{\mu\text{-}C(PPh_3)CO_2Et\}][ClO_4]$ (**21**) has been also prepared (Eq. 13) and an X-ray structural determination showed the presence of an Au···Au contact (2.892(2) Å) with an Au–C(ylide)–Au angle of 86.3(4)°. The Au–C(ylide)–Au moiety has been represented as a closed three-centre two-electron bond as suggested for other complexes containing the $Ph_3PAuAuPPh_3$ system, and points to a double role of the Ph_3PCCO_2Et ligand as ylide and bridging carbene [28](b).

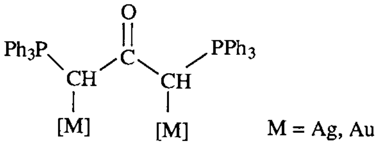


21

R = Me, Et

(13)

The extension of this type of reactivity to the diphosphonium salt $[(Ph_3PCH_2)_2CO][ClO_4]_2$ leads to the formation of a series of homo- and heterobimetallic complexes with a CCC-bridging skeleton [28](e) of the type **G**:

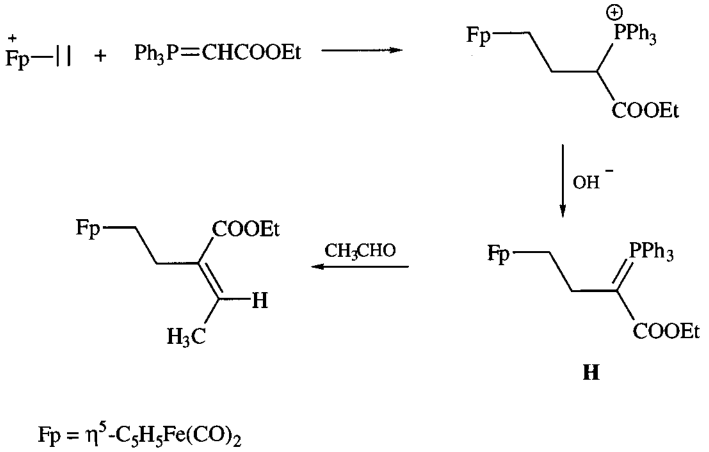


G

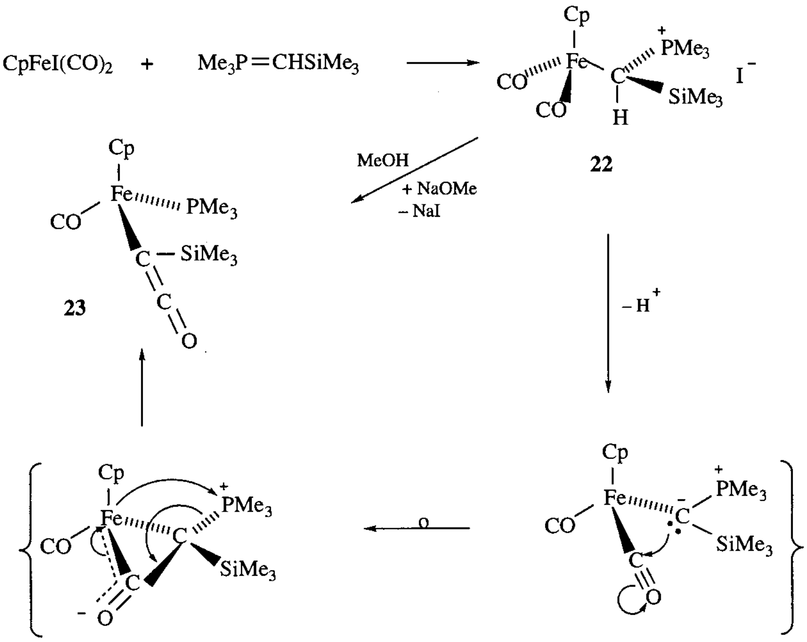
Carbonyl-stabilized ylides were reported to act as nucleophiles towards olefins coordinated to iron centers [29] to give adducts that would be useful synthetic intermediates; as a matter of fact they may be deprotonated to form, for instance, iron–ylide systems of the type **H** which can further react with aldehydes in a Wittig reaction to yield new organometallic moieties (Scheme 6).

The intermediacy of an ylidic $R_3P{=}CR'COM$ moiety has been proposed [30] in the reactions of trialkyl(alkylidene)phosphorane with metal coordinated carbon monoxide resulting in the formation of an η^1-ketenyl complex (Scheme 7).

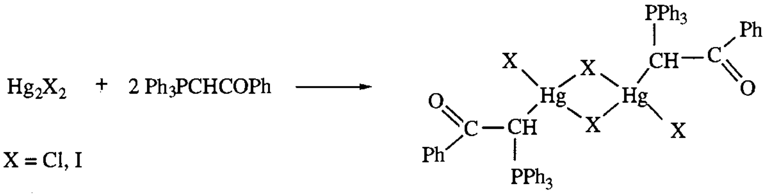
The reaction of BPPY with $[Hg_2X_2]$ (X = Cl, I) in equimolar ratio using methanol as the solvent has been reported to yield crystals of $[Ph_3PCHCOC_6H_5 \cdot HgX_2]_2$ 2 CH_3OH, where the keto-stabilized ylide is C-coordinated to the metal and the Hg–C bond lengths are 2.208(8) and 2.313(13) Å for the Cl and I complexes, respectively. The internuclear distances between the mercury atoms were found to be 3.810(2) and 4.014(1) Å for Cl and I complexes, respectively, indicating the absence of significant bonding interactions [31] (Eq. 14).



Scheme 6.



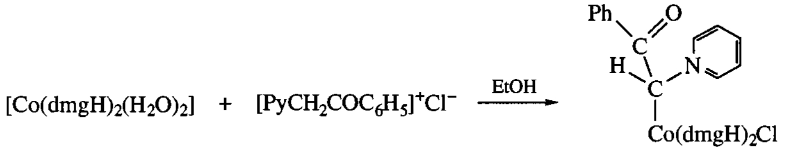
Scheme 7.



24

(14)

Finally, the synthesis of the cobalt(III)–ylide complex $[CoCl(dmgH)_2(C_5H_4NCH_2COPh)]$ has been reported to occur by reaction of $[Co(dmgH)_2(H_2O)_2]$ (dmgH = dimethylglyoxime monoanion) and $[C_5H_4NCH_2COPh]^+Cl^-$ [32] (Eq. 15). The complex has also been characterized by an X-ray structure determination which showed that the ylide ligand coordinates to cobalt through the ylide carbon with a Co–C distance of 2.07(1) Å close to the bond length of Co–C (2.04 Å) in carbomethoxymethylbis(dimethylglyoximato)(pyridine)–Co(III), one of the few alkyl cobaloxime complexes described in the literature.



(15)

dmgH = dimethylglyoxime mono anion

25

2.2. Metal–O(ylide) coordination

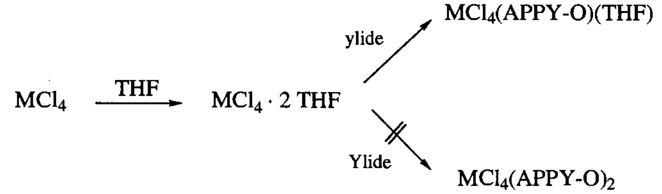
As it has been mentioned previously, very few examples of O-coordinated ylides are known [5].

The first complex with the APPY ligand O-coordinated was obtained with the very oxophilic metal center Sn(IV) [33](a). The X-ray structure determination of $[Sn(CH_3)Cl\{OC(CH_3)CHPPh_3\}]$ showed that the tin–oxygen bond distance was almost identical to that found for triphenyltin-*N*-phenyl-*N*-benzoylhydroxylamine [33](b). The ylidic skeleton is planar, with the P–C–C angle of 120.3° adopting a cisoid form.

The reactions of triorganotin and lead halides with stabilized ylides such as APPY, BPPY, CMPPY have been reported [34](a) to form complexes of different stoichiometries depending on the nature of the ylide and the groups bound to the metal. Thus, with $[Me_2SnCl_2]$, APPY and CMPPY gave adducts of the stoichiometry $[3MeSnCl_2 \cdot 4(ylide)]$, while BPPY gave the complex $[5Me_2SnCl_2\ 4\ (BPPY)]$. In all cases, the IR data (a strong absorption in the range 1465–1510 cm^{-1}, at significant lower wavenumbers with respect to the corresponding free ylides) indicate that the O-coordination occurred. Such a type of coordination was shown to occur also in the reaction of equimolar amounts of BPPY with Me_3SnCl or Ph_2SnCl_2 in CH_2Cl_2 at room temperature ($\nu(CO)$ at 1480 cm^{-1}) [34](b).

O-coordinated metal ylide derivatives have been obtained also by reaction with group XVI and XIV metal complexes. The reactions of PhCOCHZ ($Z = SMe_2$, PPh_3, NC_5H_4-*p*-Me) with $[W(CO)_5THF]$ gave $[W(CO)_5(PhCOCHZ)]$ complexes [35]. In the case of $Z = SMe_2$, the coordination occurs through the C(ylide) carbon, while for $Z = PPh_3$ and NC_5H_4-*p*-Me the carbonyl oxygen is coordinated to the metal. The corresponding 2-pyridylcarbonylmethylides $C_5H_4NCOCHZ$ ($Z = SMe_2$, PPh_3, NC_5H_4-*p*-Me) reacted with $W(CO)_6$ under UV irradiation or with $[W(CO)_5(THF)]$ to afford $[W(CO)_4(C_5H_4NCOCHZ)]$ derivatives, for which the chelation through carbonyl oxygen and pyridine nitrogen has been suggested on the basis of IR and NMR data [35].

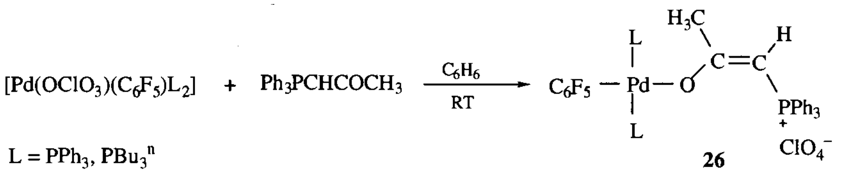
The reaction of APPY and BPPY with MCl_4 (M = Ti, Zr, Hf) has also been reported to yield *trans*-$[MCl_4(APPY\text{-}O)(THF)] \cdot THF$. For *trans*-$[TiCl_4(APPY\text{-}O)(THF)] \cdot THF$ an X-ray structure determination confirmed the O(ylide)-coordination [36] with the ylide ligand in the cisoid conformation in the solid state (Eq. 16).



(16)

M = Ti, Zr, Hf
ylide = APPY, BPPY

The first Pd(II)-O(ylide) complexes were prepared by Uson et al. [37] by reaction of APPY with the perchlorato complexes $[Pd(OClO_3)(C_6F_5)L_2]$ ($L_2 = 2PPh_3$, $2PBu^n_3$, bipy) as shown in Eq. 17.

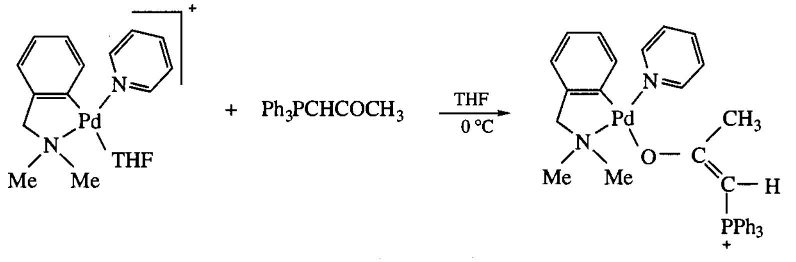


26

(17)

However, it is worthwhile noting that the neutral complex $[Pd(C_6F_5)(Cl)(tht)(APPY)]$ was obtained by reaction of APPY with the binuclear complex $[Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(tht)_2]$, where the APPY shows the usual C-coordination [37]. The C-coordination is clearly indicated by the C=O band in the IR which appears in the range 1700–1600 cm^{-1}, while the O-coordination this absorption in the range 1520–1515 cm^{-1}. Also ^1H and ^{31}P NMR data clearly distinguish between the two coordination modes, and indicate that for the O-coordinated complexes either the *cisoid* and *transoid* forms are present in solution.

Recently, the first X-ray structural determination of a Pd(II)–O(ylide) complex has been reported [5]. The complex $[Pd(dmba)(py)(APPY\text{-}O)][ClO_4]$, **27**, was obtained in high yield by reaction of a freshly prepared solution of $[Pd(dmba)(py)(THF)][ClO_4]$ (dmba = 2-((dimethylamino)methyl)-phenyl,*C',N*) with APPY (1:1 molar ratio) in THF at 0°C according to Eq. 18.

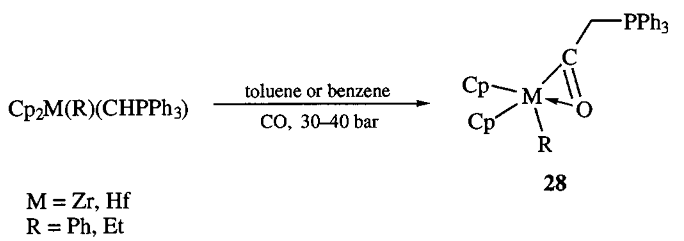


27

(18)

The IR spectrum displays a strong ν(CO) stretching at 1506 cm^{-1}. The ^1H NMR spectrum shows a doublet attributable to the methine CH proton at 4.17 ppm with a coupling constant $^2J_{PH}$ of 24 Hz, close to those reported for other O-bound complexes, but lower than those reported for C-coordinated systems. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet for **27** slightly upfield relative to the free ylide and again in agreement with the O(ylide)-coordination (the C(ylide)-coordination results in a downfield shift of ca. 10 ppm with respect to the free ylide). Finally, the $^{13}C\{^1H\}$ NMR spectrum shows the CH carbon as a doublet at a chemical shift very close to that observed in the free ylide [5]. $^1H-^1H$ 2D-NOESY experiments indicate that the O-bonded ylide adopts in solution a cisoid conformation, which has been observed also in the solid state [5]. The X-ray structure of $[Pd(dmba)(py)(APPY)][ClO_4]$ shows a Pd–O(ylide) distance of 2.154(2) Å [5].

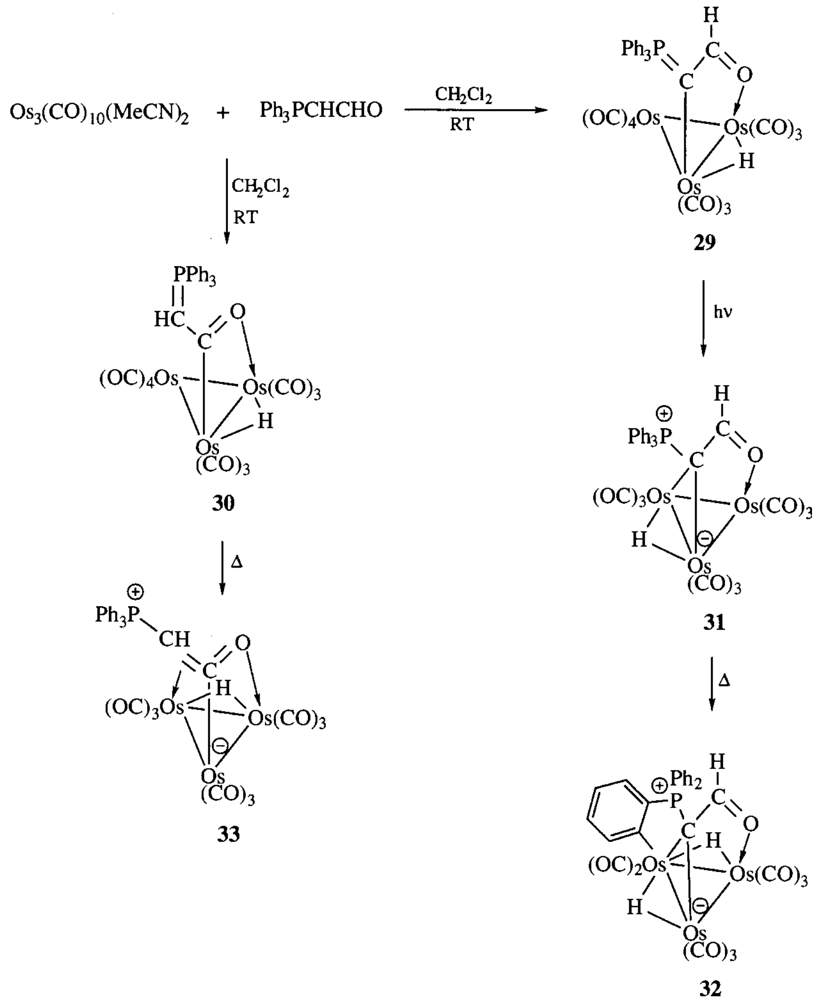
Other metal complexes containing O-coordinated ylides of the type $[Cp_2M(R)\{\eta^2\text{-}C(CHPPh_3)=O\}]$ (M = Zr, Hf) have been prepared by CO insertion into the M–C(ylide) bond in complexes of the type $[Cp_2M(C_2H_5)(CHPPh_3)]$ (R = Ph, C_2H_5). X ray determinations of $[Cp_2M(C_2H_5)\{\eta^2\text{-}C(CHPPh_3)=O\}]$ show the occurrence of M-OCCHPPh$_3$ moieties with Zr–O and a Hf–O distances of 2.192(3) and 2.185(3) Å, respectively, [38] (Eq. 19).



28

(19)

The only report on the reactivity of carbonyl stabilized ylides with metal clusters is represented by the reaction of $Ph_3PCHCHO$ with $[Os_3(CO)_{10}(MeCN)_2]$ [39] where an oxidative addition occurs to form the isomers $[Os_3(\mu\text{-}H)(\mu\text{-}$



Scheme 8.

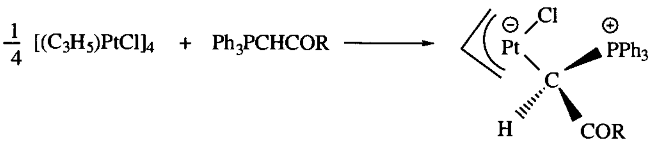
$\mathrm{Ph_3PCCHO)(CO)_{10}]}$, (**29**), and $[\mathrm{Os_3(\mu\text{-}H)(\mu\text{-}Ph_3PCHCO)(CO)_{10}}]$, (**30**), that decarbonylate to give the clusters containing triply-bridging ligands $[\mathrm{Os_3(\mu\text{-}H)(\mu^3\text{-}Ph_3PCCHO)(CO)_9}]$, (**31**), $[\mathrm{Os_3(\mu\text{-}H)_2(\mu^3\text{-}C_6H_4PPh_2CCHO)(CO)_8}]$, (**32**), and $[\mathrm{Os_3(\mu\text{-}H)(\mu^3\text{-}Ph_3PCHCO)(CO)_9}]$, (**33**), according to Scheme 8.

The X-ray structure determinations of **29** and **30** indicate that the $\mathrm{Ph_3PCCHO}$ moiety bridges two metal centers through the C and O atoms [39].

2.3. Metal–C(ylide) versus metal–O(ylide) coordination

Several reports have been recently concerned with the reactivity of various platinum group metal complexes with some P- and As-carbonyl stabilized ylides of different nucleophilicity with the aim of determining the factors that address the C(ylide)-*vs*-O(ylide) coordination mode and exploring whether P- or As-ylides behave differently toward Pt complexes.

*2.3.1. Reactions with η^3-allyl Pd(II) and Pt(*II*) systems.* The reactions of $[\mathrm{PtCl(C_3H_5)}]_4$ with APPY, BPPY and CMPPY [40] lead to the formation of complexes **34** (Eq. 20), with the carbonyl stabilized ylides C-coordinated to the metal center as indicated by their IR spectra (ν(CO) in the range 1616–1682 cm^{-1}). The ^{1}H NMR spectra show the presence of two diastereoisomers due to the coordination on the platinum center of the asymmetric ylide carbon atom and the allyl group. The CH proton of **34** gives rise to two doublets in the range 4.44–5.54 ppm flanked by ^{195}Pt satellites ($^2J_{HPt}$ 80–94 Hz).

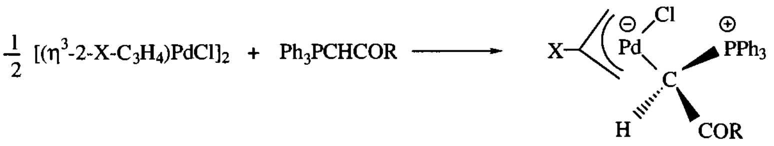


34

R = Me, **a**; Ph, **b**; OMe, **c**

(20)

Palladium(II) allyl complexes of the type [Pd(η^3-2-X-C$_3$H$_4$)Cl]$_2$ (X = H, CH$_3$) [41] behave similarly, reacting with APPY and BPPY to afford complexes **35** containing Pd–C(ylide) bonds (Eq. 21) as evidenced by IR (ν(CO) 1624–1598 cm^{-1}) and low temperature NMR data [41].



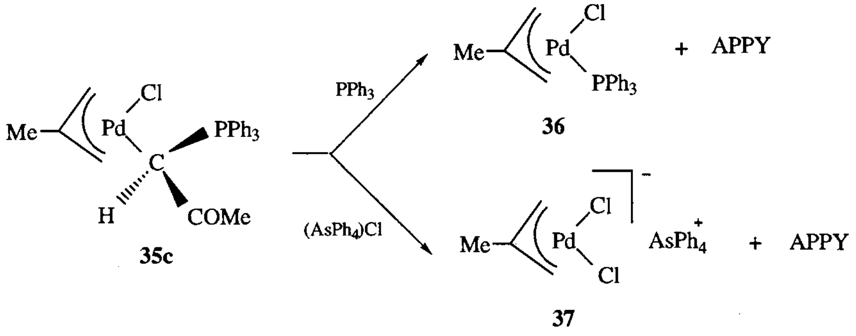
35

X = H R = Me, **a**; Ph, **b**

X = Me R = Me, **c**; Ph, **d**

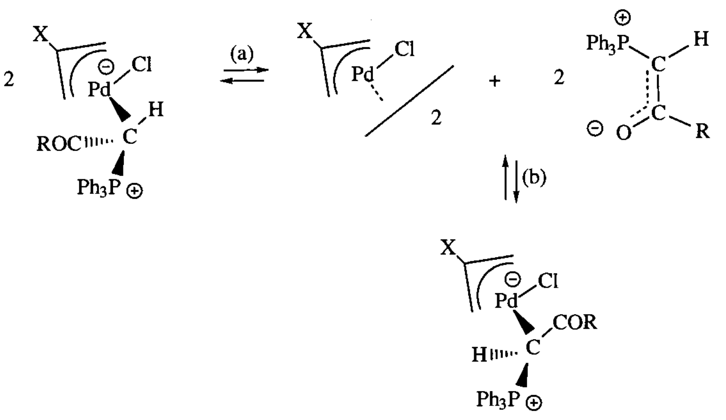
(21)

The C-coordination to the palladium center of APPY has been also confirmed by the X-ray structure determinatiom of [PdCl(η^3-2Me-C$_3$H$_4$){Ph$_3$PC(H)COMe}] [41]. The palladium center displays a distorted square planar geometry with the allyl carbons out of the coordination plane on the opposite site with respect to the phosphonium group in order to minimize the steric hindrance. The Pd–C(ylide) distance (2.193(3) Å) is significantly longer than those found for Pd–C(alkyl) bond lengths indicating a weaker metal–carbon bond and thus suggesting that the ylide can be more readily displaced by other ligands. This behaviour has been confirmed in the reaction of PPh$_3$ and [AsPh$_4$]Cl with **35c** to give the products **36** and **37**, respectively, (Eq. 22).



(22)

Spectroscopic evidence indicate that there is Pd–(ylide) bond breaking in solution giving rise to the interconversion of the diastereoisomeric forms through a dissociative mechanism (Eq. 23a) via the occurrence of the equilibrium 23b [41].

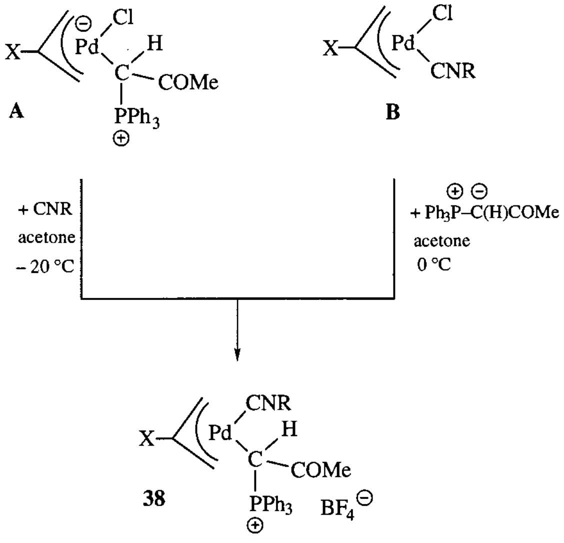


(23)

Equilibrium (23a) has been studied by UV-Vis and IR techniques [42] for $Cy_3PCHCOR$ (R = Me, OMe, Ph), $Ph_3PCHCOMe$, $Bu^t_3PCHCOMe$. The order of the log K_c values for the formation of $[Pd(\eta^3\text{-2-Me-}C_3H_4)(Cl)(PCy_3CHCOR)]$ parallels the ylide basicity order as reflected by the pK_a values of the conjugate phosphonium acids $[Cy_3PCH_2COR]Cl$ [43] (Table 1). To the higher acidity of the triphenylphosphonium salt (pK_a 8.30) corresponds the lower log K_c value (1.7 ± 0.3). In the case of $Bu^t_3PCHCOMe$ (pK_a 9.18) the log K_c value (0.65 ± 0.09) results lower than expected probably originated by a steric effect due to the much more sterically demanding Bu^t moiety. For $Ph_3PCHCOMe$ the log K_c value results higher than that of $PCy_3CHCOMe$ possibly due again to a steric effect of the two phosphonium groups with the lower cone angle of PPh_3 compared to PCy_3. These data indicate that coordination properties appear to be originated by both steric and electronic effects (see above). Replacement in complexes of the type **35** of an anionic σ-electron donating ligand such as Cl^- by a π neutral acceptor such as an isocyanide [44] ligand would be expected to stabilize the M–C(ylide) bond to a greater extent towards dissociation. Thus, the reactions reported in Scheme 9 have been carried out in order to prepare complexes **38** which do not spontaneously dissociate in solution. These experimental evidence indicate that the Pd–ylide bonds in **38** are stronger than those in complexes **35** but still weak enough to be readily replaced by Cl^- and CNR ligands. This lability is also consistent with the structural data which show a high value (2.174(9) Å) for the Pd–C(ylide) bond distance in the X-ray of the complex $[Pd(CNCMe_3)(\eta^3\text{-2-Me-}C_3H_4)Ph_3PC(H)COCH_3]\ BF_4$ [44].

Table 1
pK_α values of some ylide conjugate acids

Ylide	R	pK_α	Solvent	Ref.
$Ph_3P{=}CHCOR$	Ph	6.0	CH_3OH	[43](a)
	OEt	9.2	CH_3OH	[43](a)
$Ph_3P{=}CHCN$		7.5	CH_3OH	[43](a)
$Ph_3P{=}CHCOR$	Ph	6.0	$C_2H_5OH/H_2O(80/20)$	[43](c)
	Me	6.6	$C_2H_5OH/H_2O(80/20)$	[43](c)
	OMe	8.8	$C_2H_5OH/H_2O(80/20)$	[43](c)
	OEt	8.95	$C_2H_5OH/H_2O(80/20)$	[43](c)
	$-C_6H_4$-*p*-OMe	6.7	$C_2H_5OH/H_2O(80/20)$	[43](c)
$Ph_3P{=}CHCOR$	Ph	5.60	C_2H_5OH (95%)	[43](d)
$Ph_3P{=}CHCOR$	Ph	6.00	$C_2H_5OH/H_2O(80/20)$	[43](b)
	Me	6.65	$C_2H_5OH/H_2O(80/20)$	[43](b)
	OEt	8.85	$C_2H_5OH/H_2O(80/20)$	[43](b)
$Ph_3As{=}CHCOR$	Ph	8.65	$C_2H_5OH/H_2O(80/20)$	[43](b)
	Ph	8.55	$C_2H_5O\ H/H_2O(50/50)$	[43](b)
$Ph_3As{=}CHCOR$	Ph	8.52	in 0.1N KCl solution	[77]
	$-C_6H_4$-*p*-OMe	9.16	$C_2H_5OH/H_2O(50/50)$	[77]



X = H; R = p-C_6H_4OMe, **a**; $C(Me)_3$, **b**
X = Me; R = p-C_6H_4OMe, **c**; $C(Me)_3$, **d**; Me, **e**; C_6H_{11}, **f**; p-$C_6H_4NO_2$, **g**

Scheme 9.

2.3.2. Reactions with the Zeise's salt. The Zeise's salt reacts with one equivalent of the carbonyl-stabilized ylides $Ph_3ECHCOR$ ($E = P$, As) in MeOH [45] to form in high yield compounds **39** (Eq. 24).

$$K[PtCl_3(\eta^2\text{-}C_2H_4)] \quad + \quad \text{ylide} \quad \xrightarrow[\text{MeOH, RT}]{-\text{KCl}} \quad \underset{\textbf{39}}{trans\text{-}[PtCl_2(\eta^2\text{-}C_2H_4)(\text{ylide})]} \tag{24}$$

ylide = APPY, **a**
CMPPY, **b**
BPPY, **c**
BCyPYOMe, **d**
APAsY, **e**
CMPAsY, **f**
BPAsY, **g**

All the derivatives contain the ylide C-coordinated to the platinum center. The ${}^1J_{PtC(olefin)}$ values in complexes *trans*-$[PtX_2(olefin)L]$, where L does not show π-acid properties, can be correlated to the relative *trans* influence of the ligand L [46]. In complexes **39a–d** the ${}^1J_{PtC(C_2H_4)}$ are in the range 103–107 Hz, while in complexes **39e–g** the ${}^1J_{PtC(C_2H_4)}$ values are about 9 Hz smaller, thus indicating a somewhat higher *trans* influence of the arsonium ylides with respect to those of phosphorus. Comparing these values with those reported for other L ligands in compounds of the type $[PtCl_2(\eta^2\text{-}C_2H_4)L]$ it was possible to insert the carbonyl stabilized ylides in a series of ligands ordered according to their increasing *trans* influence: NCMe < Cl < py < NH_2R < NHR_2 $\ll$ carbonyl stabilized P-ylides < carbonyl stabilized As-ylides $\ll$ Me. The values of ${}^1J_{PtC(ylide)}$ ranging between 582 Hz for $Ph_3PCHCOPh$ to 612 Hz for $Ph_3PCHCOOMe$, appear to parallel the ylide basicity (Table 1) as reflected by the corresponding pK_a values of the conjugate phosphonium acids $[Ph_3PCH_2COR]Cl$ [43]. An analogous trend is observed for the complexes containing arsonium ylides.

Complexes **39** react (Eq. 25) with a second ylide ligand to form the bis(carbonyl-stabilized ylide)Pt(II) complexes **40**. Reaction (25) represents an easy and general method for the preparation in high yield of bis(ylide)platinum(II) complexes, containing either two identical or different ylides, both C-coordinated to the metal center.

$$trans\text{-}[PtCl_2(\eta^2\text{-}C_2H_4)(ylide)] \;+\; ylide' \xrightarrow[RT]{MeOH} trans\text{-}[PtCl_2(ylide)(ylide')]$$

40

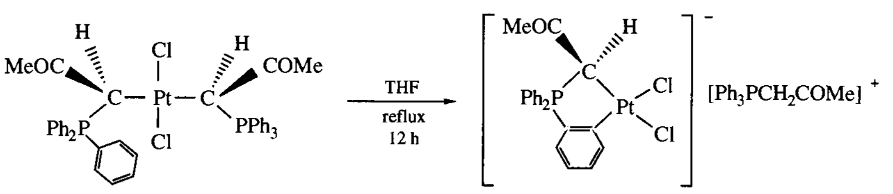
ylide = ylide' = APPY, **a**
CMPPY, **b**
BPPY, **c**
BCyPYOMe, **d**
APAsY, **e**

(25)

ylide =	ylide' =
APPY	CMPPY, **f**
APPY	BPPY, **g**
CMPPY	BPPY, **h**
CMPPY	BCyPYOMe, **i**
APPY	CMPAsY, **j**

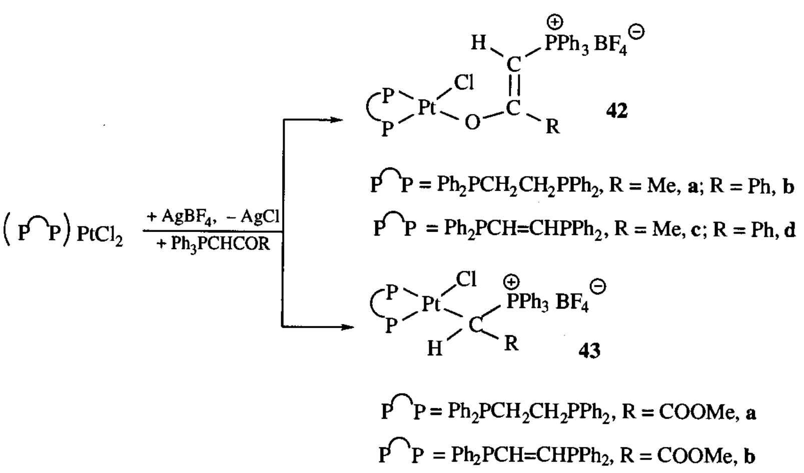
Compounds **40** are present as two diastereoisomeric forms owing to the simultaneous presence on the metal center of two asymmetric methine C atoms.

Upon refluxing overnight the complex $[PtCl_2\{CH(COMe)PPh_3\}_2]$, the cyclometalated derivative **41** was obtained (Eq. 26), which was structurally characterized [45].



40a **41** (26)

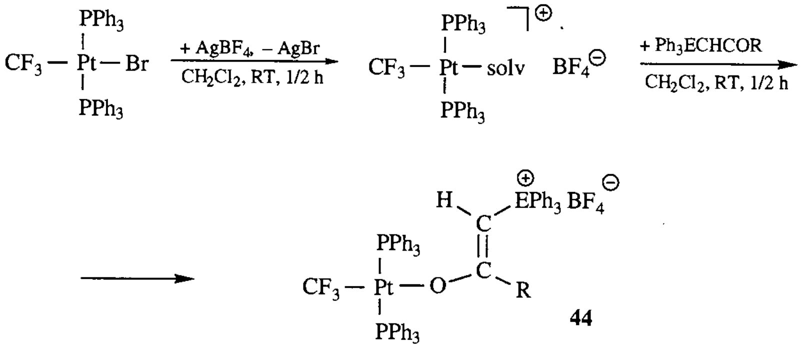
2.3.3. Reactions with cationic diphosphino Pt(II) complexes. By reacting carbonyl stabilized ylides with $[PtCl(P–P)(solv)][BF_4]$ [40] either Pt–O(ylide) or Pt–C(ylide) complexes are formed according to Eq. 27 depending on the nucleophilicity of the entering ylide.



(27)

The more nucleophilic CMPPY coordinates to Pt(II) through the ylidic carbon atom, to form complexes **43**, while APPY and BPPY lead to the formation of the O-coordinated complexes **42**, as evidenced by spectroscopic data. The IR spectra of **43a,b** show a strong CO band at 1708 and 1688 cm^{-1}, respectively, and their ^{31}P NMR spectra show the $P_{(phosphonium)}$ resonance shifted downfield by ca. 11 ppm with respect to the free ylide ($^2J_{PtP(ylide)}$ ca 100 Hz). Conversely, in the O-coordinated ylide complexes **42a–d** ν(CO) appears in the range 1515–1500 cm^{-1}, at lower wavenumbers with respect to the free ylide, while the ^{31}P NMR spectra show the $P_{(phosphonium)}$ resonance slightly shifted upfield relative to the free ylide.

2.3.4. Reactions with trans-[Pt(CF$_3$)(PPh$_3$)$_2$(solv)][BF$_4$]. Selective O-coordination has been observed in the reaction of *trans*-[Pt(PPh$_3$)$_2$(CF$_3$)(solv)][BF$_4$] with some carbonyl stabilized ylides according to Eq. 28.



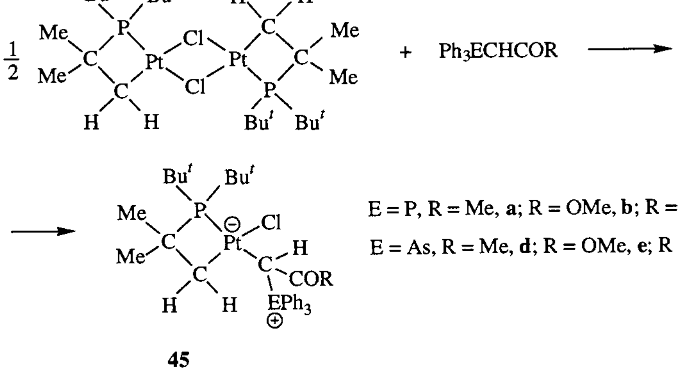
44

(28)

E = P; R = Me, **a**; R = OMe, **b**; R = Ph, **c**
E = As; R = Me, **d**

The IR spectra of complexes **44** display a strong carbonyl absorption in the range 1500–1520 cm^{-1} indicating the O-coordination of the ylide, which is also supported by ^{1}H, ^{13}C and ^{31}P NMR data. The X-ray structural analysis of *trans*-[Pt(CF$_3$)(PPh$_3$)$_2${OC(OCH$_3$)=C(H)(PPh$_3$)}][BF$_4$] represents the first report of a Pt–O(ylide) complex. The Pt–O(ylide) distance is 2.093(3) Å, longer than those reported for Pt–OH(terminal) (ca. 2.006 Å), Pt–O(alkoxy terminal) (ca. 2.028 Å) [47](a) and than that observed in the peroxo complex *trans*-[PtPh(PPh$_3$)$_2$(OOBu^t)] [47](b). The carbomethoxymethylene system O–C–C–P adopts a cisoid conformation forcing the CH proton to point towards the metal with a Pt···H non bonding interaction of 2.94 Å.

2.3.5. Reactions with [PtCl{P(Bu^t)$_2$C(Me)$_2$CH$_2$}]$_2$. The effect of the steric hindrance of the ancillary ligands at the platinum metal center on the coordination mode of some carbonyl stabilized ylides could be evidenced in their reactions with the dimeric complex [PtCl{P(Bu^t)$_2$C(Me)$_2$CH$_2$}]$_2$, where the –P(Bu^t)$_2$ group of the chelate P–C ligand is much more sterically encumbered of the CH$_2$ moiety [40]. Although the bridge splitting of this dimer by some P- and As-carbonyl stabilized ylides could give four different isomers, the only isolated product was the C-coordinated derivative bearing the ylide in *cis* position to the less hindered –CH$_2$ moiety according to Eq. 29.



45

E = P, R = Me, **a**; R = OMe, **b**; R = Ph, **c**
E = As, R = Me, **d**; R = OMe, **e**; R = Ph, **f**

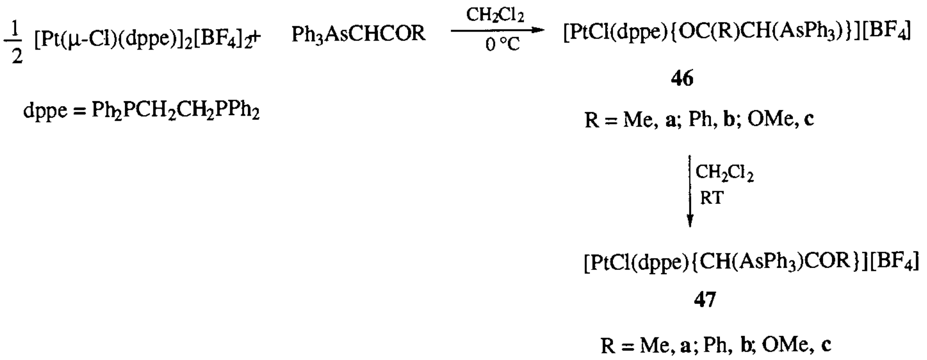
(29)

The IR spectra of complexes **45** show the CO absorption in the range, 1609–1677 cm^{-1}, as expected for C-coordination. NMR data support the proposed structure; in particular, the ^{31}P NMR spectra of **45** show the signal of P_{ylide} as a doublet in the range 24.4–26.8 ppm ($^3J_{PP}$ ca. 10 Hz) flanked by ^{195}Pt satellites ($^2J_{PPt}$ ca. 50 Hz).

Taken all together, the metal–C(ylide) versus metal–O(ylide) coordination described in reactions (20–29) can be explained by a balance of steric and electronic effects. For the less sterically demanding ‘M(η^3-allyl)Cl’ (M = Pd, Pt) fragment the reactions with carbonyl stabilized ylides yield selectively the C-bonded derivatives. In the case of the ‘(diphosphine)PtCl’ moiety, where the diphosphine ligand exhibits a higher steric hindrance than the allyl group, only the more nucleophilic ylide $Ph_3PCHCOOMe$ is able to coordinate via *C* to the Pt center, while the less nucleophilic $Ph_3PCHCOR$ (R = Me, Ph) ylides are bonded to the metal through the less hindered carbonyl oxygen atom. Accordingly, for the Pt(**II**) complexes containing the chelating $P(Bu^t)_2C(Me)_2CH_2$ ligand the ylides C-coordinate *cis* to CH_2, i.e. *cis* to the less hindered coordination site.

The selective O-coordination has been observed with the larger *trans*-$[Pt(CF_3)(PPh_3)_2]^+$ fragment. In this case, similarly to what previously was observed for $[Pd(dmba)(py)\{OC(CH_3)=C(H)PPh_3\}]^+$ [5], the cationic character of the metal complex makes the metal center ‘less soft’ and more receptive to possible coordination by a ‘hard’ ligand.

The reactions of $[Pt(\mu\text{-}Cl)(dppe)]_2[BF_4]_2$ with $Ph_3AsCHCOR$ (R = Me, Ph, OMe) [48] were reported to give at 0°C immediate formation of the complexes $[PtCl(dppe)\{OC(R)CH(AsPh_3)\}][BF_4]$, where the ylides are O-coordinated to the metal.

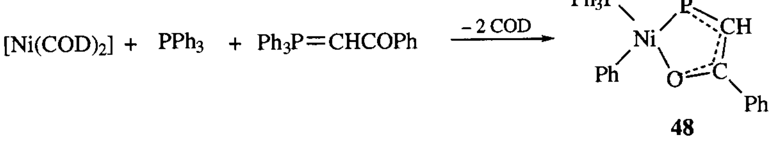


(30)

Complexes **46** are not stable in chlorinated solvents and slowly undergo isomerization to their C-coordinated analogs **47**. A kinetic study indicates that the isomerization reaction proceeds through either intramolecular or free-ylide promoted intermolecular paths with K_{obs} values of the whole process depending on the basicity of the ylide [48].

2.4. Chelating systems

The most important progress made in the carbonyl stabilized ylide organometallic chemistry has been obtained in the area of polymerization catalysis [1,49]. Since 1978 Keim [50] reported the synthesis of phenyl nickel(II) complexes **48** containing chelate P,O-ligands by reaction of $[Ni(COD)_2]$ (COD = 1,5-cyclooctadiene) with BPPY in the presence of PPh_3 (Eq. 31).



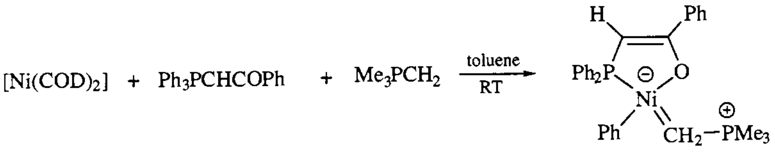
(31)

A similar reaction has been described for $Ph_3As{=}CHCOPh$ to give $[\overline{\mathrm{Ni(OCPhCHA}}\mathrm{sPh_2)(Ph)(PPh_3)}]$ [50](b).

Complex **48** has been reported to give stoichiometric insertion of CO_2 and CO_2/C_2H_4 forming, after esterification with MeOH, hydrocynnamic acid methyl ester, methyl benzoate, styrene, ethylbenzene and *n*-butylbenzene [50]. It is also highly active in the linear oligomerization of ethylene [50(a)] affording at 50 bar and 50°C up to 99% linear C_{30} with an activity of 6000 moles of ethylene per mole of complex. High molecular weight linear polyethylene is obtained performing the reaction in *n*-hexane. The catalyst can be regarded as a model for the SHOP (Shell’s Higher Olefins Process) system in which α-linear olefins for detergents are obtained by ethylene oligomerization [51].

Complex **48** has been heterogenized resulting in a modification of the catalytic properties [52]. Binding **48** over the phosphinated polystyrene or a P,O-chelate ligand oligomerized ethylene to 99% linear α-olefins; conversely, impregnation on silica and silica–alumina produced enhanced double-bond isomerization in the products.

The reaction of [Ni(COD)$_2$] with BPPY and Me$_3$PCH$_2$ in toluene (Eq. 32) yielded a highly active homogeneous catalyst for the polymerization of ethylene. At 10 bar and 90°C, complex **49** catalyzes the oligomerization of ethylene with an activity of ca. 0,5·10^5 moles of ethylene per mole of complex [53].

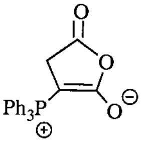


49

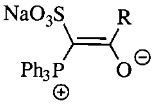
(32)

By tuning the ligands it is possible to obtain oligomers as well as high-molecular-weight polymers. It is widely accepted that the chelate P,O part of the complex controls the selectivity of the reaction, while the organic part stabilizes the complex. In situ NMR studies are consistent with the fact that the active species in the ethylene oligomerization is a nickel hydride species [51].

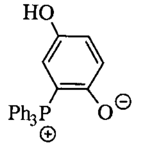
Similar bis(ylide)nickel systems Ni^0/Ph$_3$PCR^{1}CR^{2}O/R$^3_3$PCR^{4}R^5 (R^1 to R^5 = alkyl and aryl groups or heteroatom substituents) are efficient catalysts for ethylene oligomerization and polymerization, as well as for the copolymerization of ethylene with α-olefins [53]. In particular, high density polyethylene (HDPE) and ultra-high molecular weight polyethene (UHMW-PE) with M > 10^6 g mole^{-1} can be achieved using new bis(ylide) nickel catalysts containing the three ligands **I–K** [53](b).



I



J

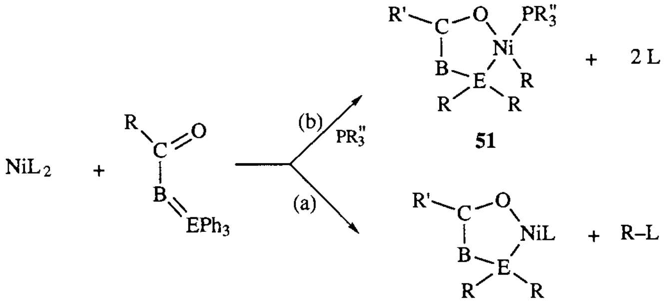


K

This type of bis(ylide)nickel complexes has been also reported to catalyze the polymerization of acetylene [53](c).

The X ray structure determination of the bis(ylide)nickel catalyst [$\overline{\mathrm{NiPh(Ph_2PCHCMeO}}$)i-Pr$_3PCH_2$] [54] confirmed the presence of a structurally intact C-coordinated i-PrPCH$_2$-ylide ligand in the *trans* position to the diphenylphosphino group of a Ph$_2$PCHCMeO–P chelate moiety with a Ni–O bond length of 1.95 Å.

Reaction (31) has been extended to a series of α-ketoylides [55] of phosphorus and arsenic Ph$_3$E=BCOR (E = P, As; B = CH, CR′, N) to give a variety of nickel complexes. Depending on the nature of the Ni(0) compounds, the phenyl group migrates to the hydrocarbon ligand to form the C–C linked hydrocarbon R–L product (route *a* in Eq. 33) or migrates to the nickel atom forming a nickel–phenyl bond (route *b* in Eq. 33).



50

L = COD, C$_3$H$_5$, C$_4$H$_7$, C$_5$H$_5$
B = CR, N, CH
E = P, As

(33)

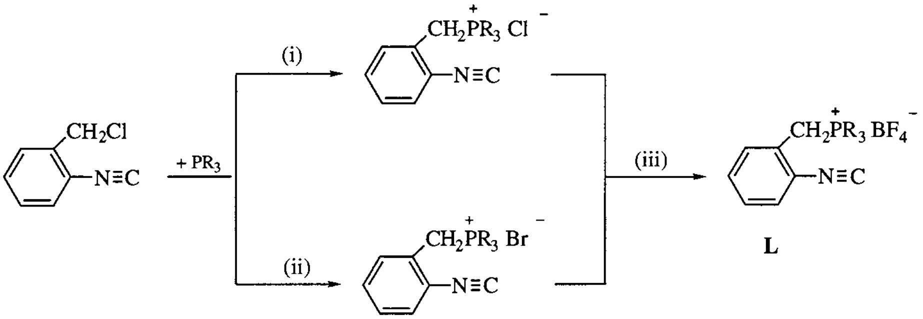
The Ni–Ph bond in **51** proved to be reactive toward insertion of CO, CO_2, C_2H_4 and PhC≡CPh, yielding in the case of PhC≡CPh and CO products which are active catalyst precursors for the oligomerization of C_2H_4 to highly linear α-olefins [55].

3. Phosphonium functionalized isocyanides and their corresponding ylides

Phosphonium-substituted isocyanide ligands of the type **L** (Scheme 10) were readily obtained in nearly quantitative yield by reacting the (halomethylphenyl)isocyanide precursor with a slight excess of the appropriate phosphine [56]. The crystalline isocyanide ligands $\mathbf{L_1}$–$\mathbf{L_4}$, which are stable either as solids and in solution, readily coordinate to some cationic Pt(II) species as shown in Scheme 11. All the complexes **52**–**54** display a significant increase of the C≡N absorption suggesting a high electrophilic character for the isocyanide carbon and therefore its potential ability to react with nucleophiles to give carbene derivatives. All the complexes (except **53c**) of Scheme 11 undergo a fast reaction at room temperature upon treatment with a 10-fold excess of a mild base such as triethylamine, affording the cyclic ylide-functionalized carbene complexes [56] depicted in Scheme 12. The cyclization mechanism involves an initial attack of NEt_3 on the activated methylene group of the phosphonium moiety to produce the highly reactive ylide–isocyanide–Pt(II) intermediate **M**, which rapidly rearranges to the cyclic intermediate **N** by intramolecular nucleophilic attack of the ylide methine to the coordinated isocyanide carbon. The final indolidin-2-ylidene product **55** is obtained by proton shift from the phosphonium group of intermediate **N** to the nitrogen atom which can take place either intramolecularly or by the assistance of the $NEt_3/NHEt_3^+$ system acting as a proton transfer agent.

The ‘ylide–carbene’ compounds **55a**–**f** are stable in the solid state and in solution and their structures have been fully established by IR, ^1H and $^{31}P\{^1H\}$ NMR spectroscopies [56]. Qualitative observations of the reaction times for the cyclization reactions, based on monitoring the $\nu_{(NC)}$ disappearance in the IR of the precursors **52**–**54** lead to the following order of reactivity **54** > **52** > **53.** This order parallels also the values of the corresponding $\Delta\nu = \nu(N{\equiv}C)_{coord} - \nu(N{\equiv}C)_{free}$ shifts [57], which reflect the electrophilic character [58] of the isocyanide carbon and therefore its ability to react with nucleophiles to form carbene complexes [59].

An X-ray structure determination was carried out for the complex *trans*-$[PtCl\{=\overline{CN(H)\text{-}o\text{-}C_6H_4C}PMe_3)\}(PPh_3)_2]$ $[BF_4]$ (55). The indole plane is strictly perpendicular to the Pt(II) coordination square. Bond lengths within the condensed system indicate extensive electronic delocalization (C–C average 1.40(2) Å; C–N, average 1.38(1) Å) [60]. The C(carbene)–C(ylide) bond distance of 1.41(1) Å is longer than those found for other related bond lengths in ylide–carbene complexes of the type $[(CO)_5Cr(OSiMe_3)CHPMe_3]$ (1.332(9) Å) [61], $[Cp(CO)_2Mn(CO_2Me)CHPPh_3]$



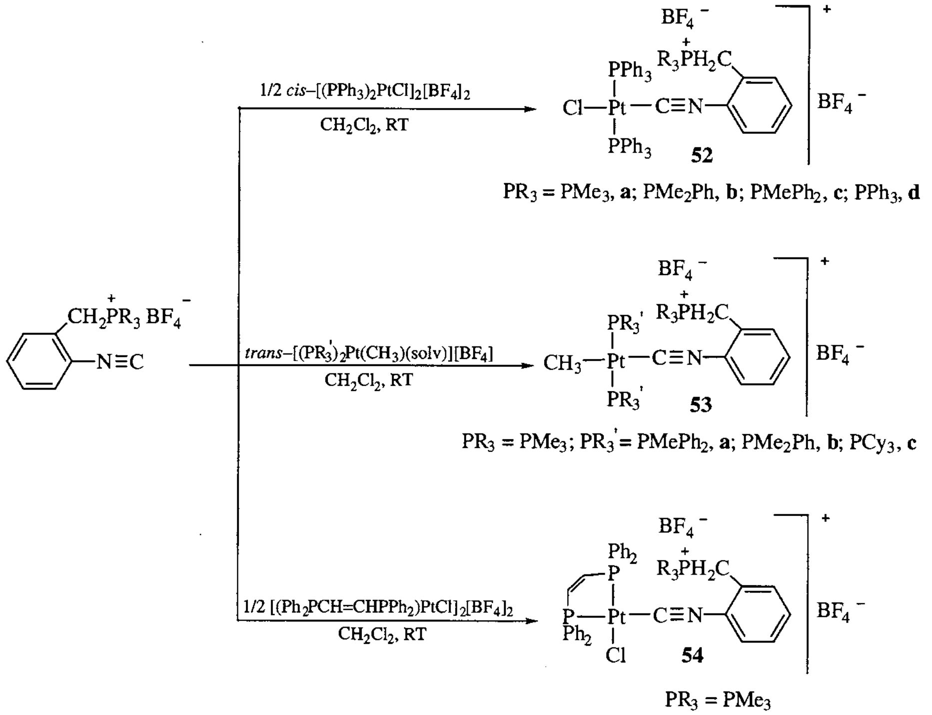
$PR_3 = PMe_3$, $\mathbf{L_1}$; PMe_2Ph, $\mathbf{L_2}$; $PMePh_2$, $\mathbf{L_3}$; PPh_3, $\mathbf{L_4}$

(i) CH_2Cl_2, RT; + $PR_3 = PMe_3$, PMe_2Ph

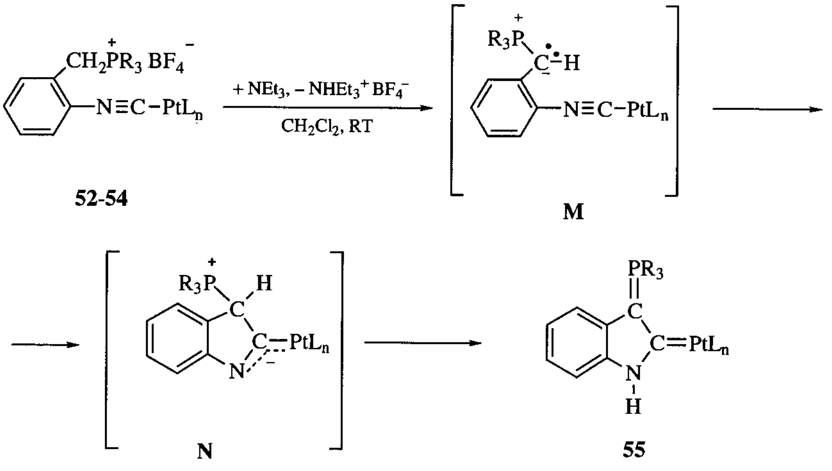
(ii) acetone, RT; + $PR_3 = PMePh_2$, PPh_3; + LiBr (exc);– LiCi

(iii) acetone, RT; + $NaBF_4$ (exc), – NaX (X = Cl, Br)

Scheme 10.



Scheme 11.



PtL_n = *trans*-$[(PPh_3)_2PtCl][BF_4]$; $PR_3 = PMe_3$, **a**; PMe_2Ph, **b**; $PMePh_2$, **c**; PPh_3, **d**

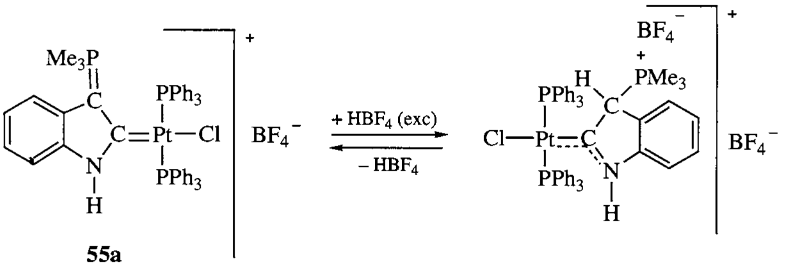
PtL_n = *trans*-$[(PMePh_2)_2Pt(CH_3)][BF_4]$; $PR_3 = PMe_3$, **e**

PtL_n = *trans*-$[(PMe_2Ph)_2Pt(CH_3)][BF_4]$; $PR_3 = PMe_3$, **f**

PtL_n = *cis*-$[(Ph_2CH{=}CHPPh_2)PtCl][BF_4]$; $PR_3 = PMe_3$, **g**

Scheme 12.

(1.361(4) Å) [62], and $[Cp(CO)_2MnC(OMe)C(Me)PMe_3]$ (1.386(14) Å) [63]. The carbene ligand in complex **55** shows the typical reactivity of indoles [64] reacting with electrophiles such as HBF_4 to give proton addition at the β-position of the indole ring [56] (Eq. 34).


55a

(34)

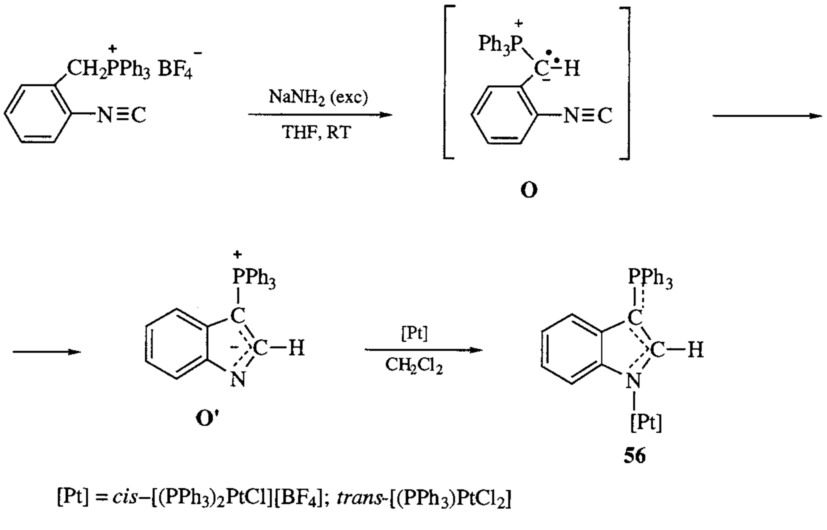
A metal-free indolyl product **O'** was obtained in an attempt to isolate the free ylide–isocyanide ligand o-$(R_3\overset{+}{P}\overset{-}{C}H)C_6H_4NC$, (**O**), (Scheme 13) [56]. The 3-(triphenylphosphonium)indolyl derivative was prepared reacting $\underline{o}$-$(BF_4^- Ph_3P^+CH_2)C_6H_4NC$ using an excess of a strong base such as $NaNH_2$ in THF at room temperature while no reaction occurs with an excess of NEt_3 in CH_2Cl_2 after several days. The indole structure has been further confirmed by coordination to Pt(II) substrates resulting in the formation of Pt(**II**)-indole derivatives in which the Pt atom is bonded to the nitrogen atom of the indole ring [56].

The reactivity of Pt(II)-coordinated benzyl-phosphonium-substituted isocyanide complexes of the type **57** is summarized in Scheme 14 [65]. By reaction with NEt_3 either one of the ylidic carbanions **P** and **P′** can be formed, which undergo subsequent ring closure to give complexes **58** and **59**, respectively. On the other hand, by reaction with NEt_3 the ylidic intermediate **P** was selectively formed as evidenced by the formation of only **58**-type complexes, one of which (**58b**) was structurally characterized.

The $-CH_{2b}$ protons of **58** (Scheme 14) react further with a stronger base such as KOH fo form the platina-heterocycle **60** by nucleophilic attack of the ylidic carbanion in the intermediate **Q** on the metal center with loss of a PPh_3 ligand (Scheme 15). Chloride abstraction by Ag^+ from complex **60** and subsequent treatment with OH^-, CO, PPh_3, yields the corresponding hydroxo (**61**) carbonyl (**62**), and phosphine (**63**) derivatives, respectively.

Cyclization reaction of phosphonium-substituted phenyl isocyanides may occur also with low-valent metal complexes of these ligands, thus giving an entry to metal(0) heterocyclic carbenes [66]. Pentacarbonyl isocyanide complexes of Cr(0), Mo(0) and W(0) are prepared in acetone at room temperature by metathesis reactions starting from $[M(CO)_5I][NEt_4]$, $AgBF_4$, and the appropriate ligands $\mathbf{L_1}$, $\mathbf{L_4}$ and $[o$-$PPh_2(CH_2Ph)PCH_2C_6H_4NC][BF_4]$ ($\mathbf{L_5}$), as outlined in Scheme 16. In the IR spectra, the N≡C absorption appears as a medium-intensity band at a slightly higher wavelength (12–18 cm^{-1}) with respect to that of the corresponding free isocyanide ligands.

The cyclization reactions of the derivatives **64–66** are carried out in THF using stoichiometric amounts of $Na[N(SiMe_3)_2]$ as the base (Scheme 17). The deprotonation reaction (i) of Scheme 17 forms the ylide functionality of the intermediate species **R**, which then gives the intermediate **S** by intramolecular attack on the coordi-

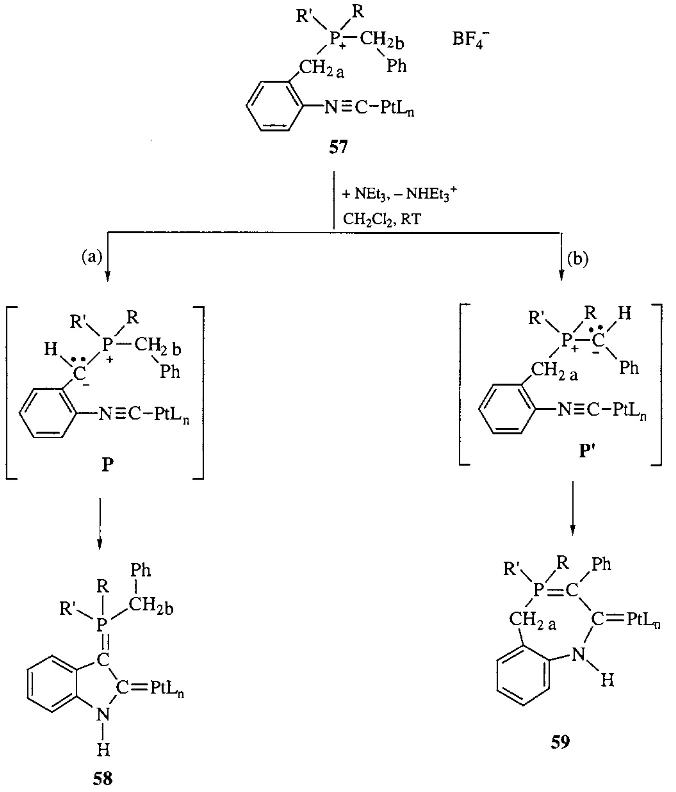

O

O'

56

[Pt] = cis-$[(PPh_3)_2PtCl][BF_4]$; $trans$-$[(PPh_3)PtCl_2]$

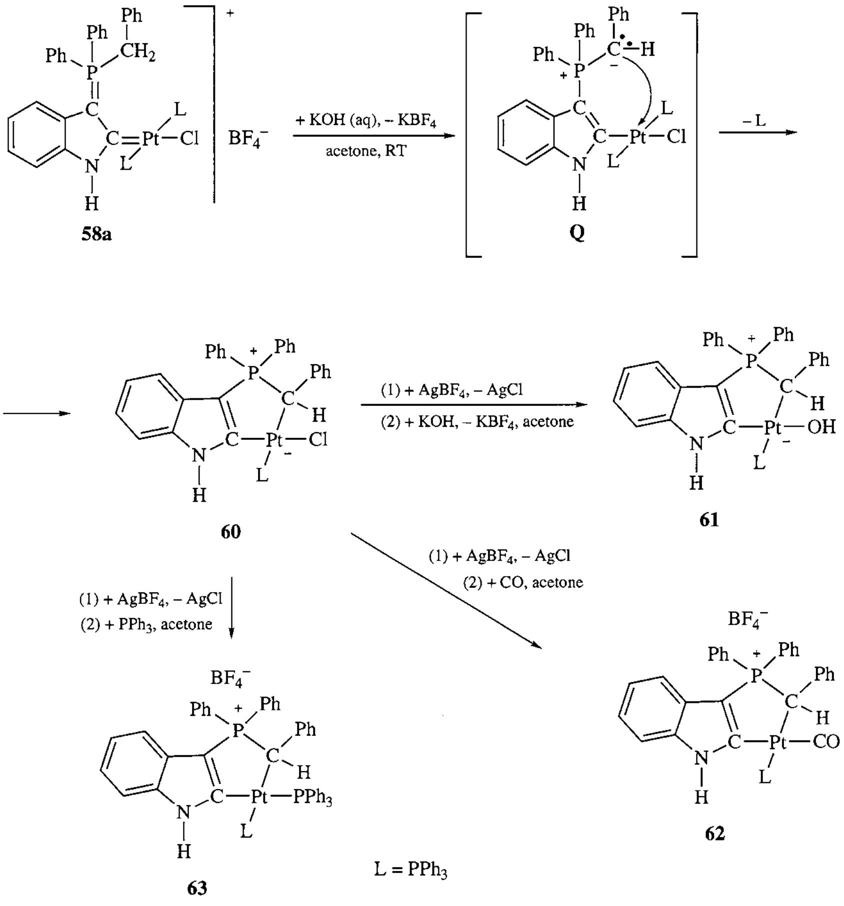
Scheme 13.



PtL_n = *trans*-$[PtCl(PPh_3)_2]^+[BF_4]^-$

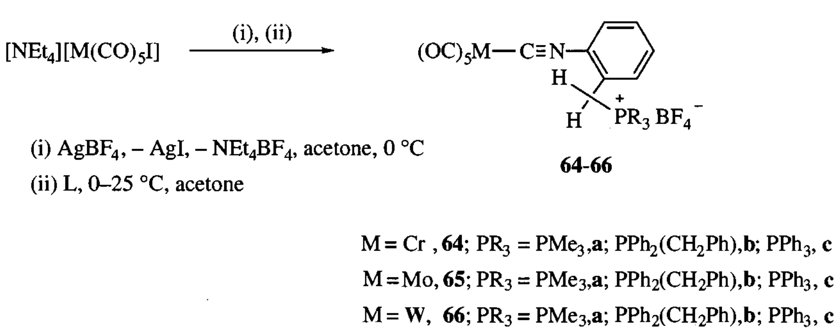
R = R' = Ph, **a**; R = Ph, R' = CH_2Ph, **b**; R = R' = CH_2Ph, **c**

Scheme 14.



L = PPh_3

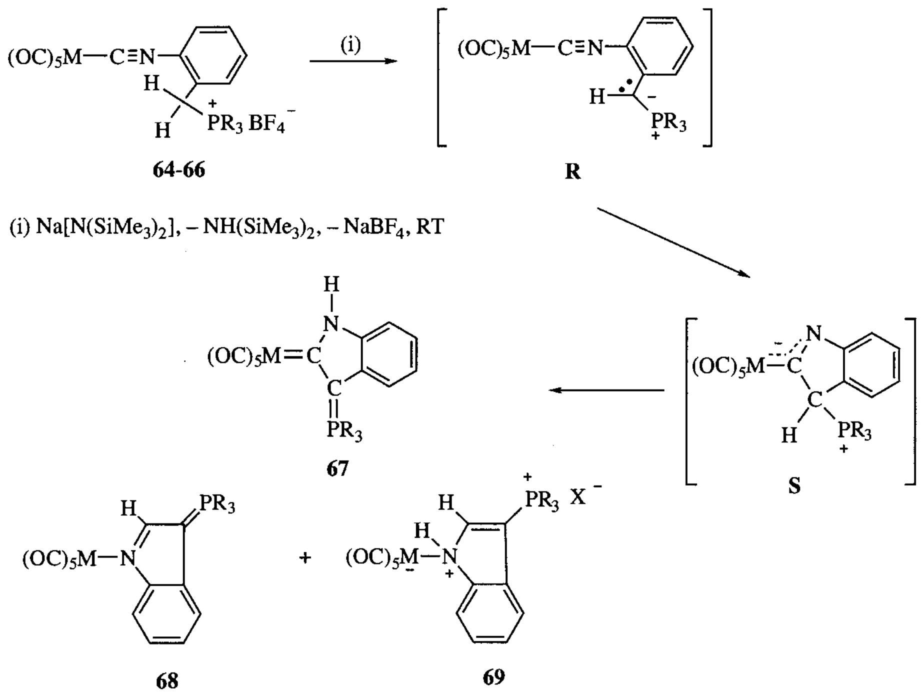
Scheme 15.



(i) $AgBF_4$, – AgI, – NEt_4BF_4, acetone, 0 °C
(ii) L, 0–25 °C, acetone

M = Cr, **64**; PR_3 = PMe_3,**a**; $PPh_2(CH_2Ph)$,**b**; PPh_3, **c**
M = Mo, **65**; PR_3 = PMe_3,**a**; $PPh_2(CH_2Ph)$,**b**; PPh_3, **c**
M = W, **66**; PR_3 = PMe_3,**a**; $PPh_2(CH_2Ph)$,**b**; PPh_3, **c**

Scheme 16.



(i) $Na[N(SiMe_3)_2]$, – $NH(SiMe_3)_2$, – $NaBF_4$, RT

Scheme 17.

nated isocyanide carbon. The proton shift from the phosphonium group to the imino nitrogen of intermediate **S** may account for the formation complexes **67** (Scheme 17).

The success of this transformation can be related to the stability of the M–C bond in the intermediate **S**, which, for group 6 metal complexes, varies as follows: W > Cr > Mo [67]. Thus, the high W–C bond strength in the cyclic intermediate could favour the 1,3-proton shift from the ylide carbon to the nitrogen atom with the formation of the carbene complexes **67**. In the case of isocyanide complexes of Cr and Mo, IR and NMR data suggest that the mainly heterocyclic system formed has a type **68** structure (Scheme 17). A possible pathway leading to the formation of the metal N-coordinated indolyl species **68** and **69** may involve a concerted mechanism with M–C bond breaking and 1,2-hydrogen shift from the ylidic to the carbene carbon.

4. The organometallic chemistry of Ph_3PCCO

The phosphacumulenes $R_3PC{=}C{=}CX$ (X = O, NR_2, S) are a particular type of stabilized ylides [68]. At the best of our knowledge, only ketenylidenetriphenylphosphorane, Ph_3PCCO, and thioketenylidenetriphenylphosphorane, Ph_3PCCS, [69] have been allowed to react with organometallic systems, giving mainly metal–ketenyl or –thioketenyl derivatives.

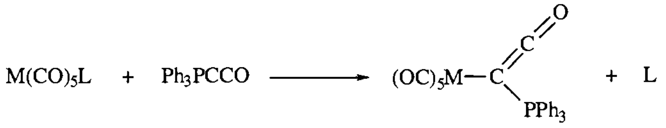
Ketenyl compounds are known for several transition metals and can be formed by different routes [70], which typically consist in a ligand-induced CO migration to a carbyne ligand or insertion of carbon suboxide, C_3O_2, into metal–hydride bonds. A wider availability for ketenyl complexes could allow the development of these complexes as useful synthetic reagents. It is noteworthy that ketene, ketenyl and ketenylidene complexes are thought to be involved in Fischer–Tropsch processes and mononuclear derivatives can be assumed as models for these systems [70](b).

Ph_3PCCO has been first obtained in 1968 by thermal decomposition of the inner salt $(Ph_3P)_2C^+-COO^-$ [69](a). The synthesis was then improved by Bestmann et al. in 1980 [69(c)], by treating $Ph_3PCHCOOMe$ with $[(Me_3Si)_2N]Na$, according to Eq. 35.

$$Ph_3PCHCOOMe + NaN(SiMe_3)_2 \xrightarrow[80\,^{\circ}C]{C_6H_6} Ph_3PCCO + NaOMe + (Me_3Si)_2NH \qquad (35)$$

The reactivity of Ph_3PCCO is different from that of ketenes, $RR'C=C=O$; for example it shows no tendency to dimerization, which is typical of ketenes and this can be explained on the basis of the different electronic structures [68].

The IR spectrum (KBr) of Ph_3PCCO is characterized by a strong CO absorption at 2080 cm^{-1} [69](c). The ^{31}P NMR spectrum shows a singlet at 5.37 ppm [69](c) and the ^{13}C NMR spectrum [71] shows the P–C carbon resonance at 2.84 ppm (d, $^1J_{CP}$ 190.0 Hz) and the C=O signal at 145.57 ppm (d, $^2J_{CP}$ 44.1 Hz). The X-ray structure of Ph_3PCCO [69](c) shows the C–C, the C–O and the C–P bond lengths of 1.210, 1.185 and 1.648 Å, respectively. A charge distribution calculation on the model molecule H_3PCCO indicates that the negative charge is localized much more on the ylidic carbon (−0.568) than on the oxygen atom (−0.282) [71], suggesting that the former is the preferred site for metal coordination. Thus, Ph_3PCCO has been reported to react with complexes of Cr, W and Mo containing labile ligands, yielding η^1-ketenyl ylidic derivatives according to Eq. 36 [72].



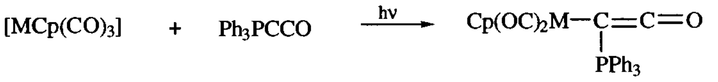
70

(36)

M = Cr, W; L = MeCN

M = Mo; L = CO

With complexes of the type $[M(Cp)(CO)_3]$ (M = Mn, Re), photolysis is needed to promote the elimination of CO (Eq. 37) [73].

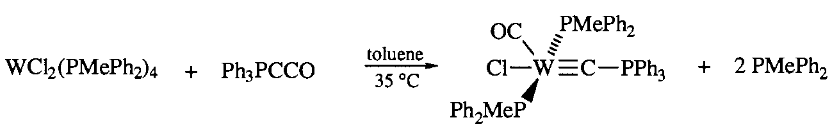


$$[MCp(CO)_3] + Ph_3PCCO \xrightarrow{hv} Cp(OC)_2M-\underset{PPh_3}{C}=C=O \qquad (37)$$

71

With $Fe_3(CO)_{12}$ different compounds are obtained [73] depending on the reaction temperature, as reported in Scheme 18. The structure of complex **73**, which was obtained at high temperature conditions, was determined by X-ray diffraction [73].

A different behaviour was observed in the reaction of $[WCl_2(PMePh_2)_4]$ with Ph_3PCCO, as reported in Eq. 38 [74].



(38)

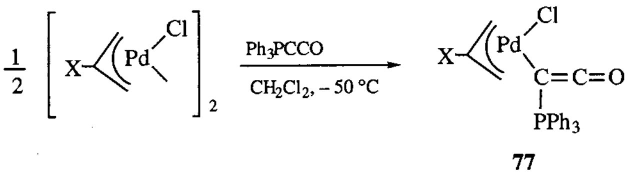
74

The carbyne derivative **74** is obtained upon cleavage of the C=C double bond of the ylide, a process that is likely assisted by the metal and represents the reverse reaction of the CO insertion into a metal–carbyne bond to give a ketenyl derivative [70]. It is interesting to note that the same carbyne derivative is obtained by reacting $[WCl_2(PMePh_2)_4]$ with carbon suboxide, C_3O_2 [74] (Scheme 19). The reaction entails the initial formation of the intermediate η^2-ketenyl ylidic derivative **75**, characterized also by an X-ray crystal structure determination [74].

More recently, the reactivity of Ph_3PCCO has been extended to Pt(II) and Pd(II) systems [70] affording η^1-ketenyl ylidic derivatives, as shown for instance in Scheme 20. Halide abstraction by a silver salt from allyl-Pd(II) or Pt(II)-complexes affords the corresponding cationic solvento species which readily react with 1 equiv of Ph_3PCCO to yield the η^1-ketenyl derivatives **76**.

The palladium derivative is stable in solution only at low temperature, while the higher thermal stability of the platinum compound allowed its complete characterization, also by a single-crystal X-ray determination, which represents the first structural report for this type of ligand. The geometry around the Pt(II) metal center is about square planar, assuming the allylic moiety as a bidentate ligand. The geometrical parameters of ketenylidenetriphenylphosphorane are not significantly changed by coordination on platinum as observed in the C–C and C–O bond lengths of 1.280(8) and 1.160(8) Å, respectively, and P–C–C (118.0(9)°) and O–C–C, (175(1)°) bond angles, which are close to the values reported for the free ylide [69](b).

Ph_3PCCO was found to be nucleophilic enough to react with $[Pd(\eta^3\text{-}2\text{-}R\text{-}C_3H_4)Cl]_2$ (R = H, Me) yielding η^1-ketenyl derivatives upon chloride-bridge splitting (Eq. 39).



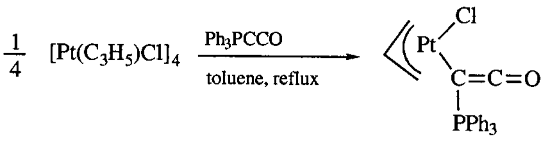
77

X = H, **a**; Me, **b**

(39)

Also derivatives **77** are stable in solution only at very low temperature.

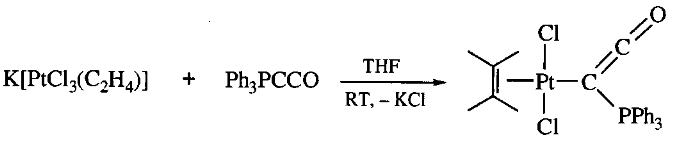
The reaction of Ph_3PCCO with $[PtCl(C_3H_5)]_4$ in refluxing toluene resulted in the formation of the complex **78** according to Eq. 40 [75].



78

(40)

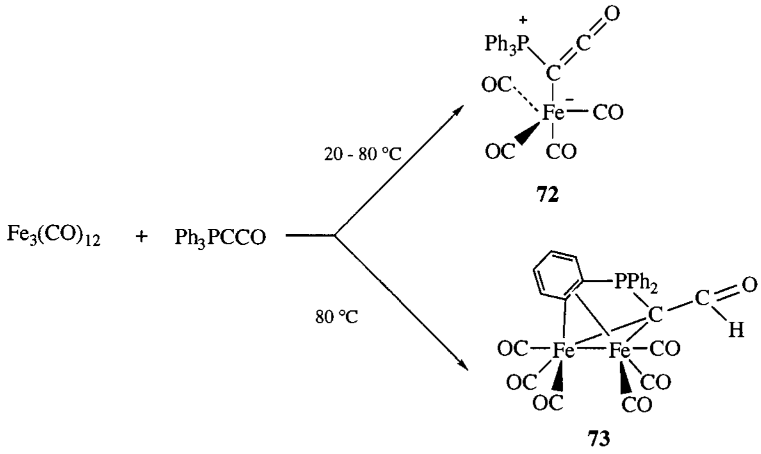
Ph_3PCCO was also found to displace a chloride ligand in the Zeise's salt, resulting in the formation of the η^1-ketenyl ylidic Pt(*II*) derivative **79**, according to Eq. 41 [75].



79

(41)

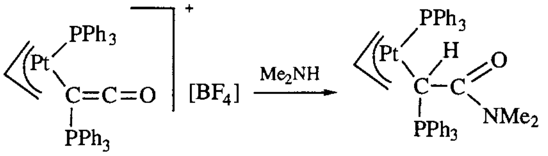
The most evident feature for η^1-ketenyl ylidic derivatives **70**, **71** and **77–79** is represented by the values of $\nu_{(CO)}$, which fall at ca. 2080 cm^{-1}, close to that of ν(CO) of free Ph_3PCCO, indicating that the ketenyl features of the ylide



Scheme 18.

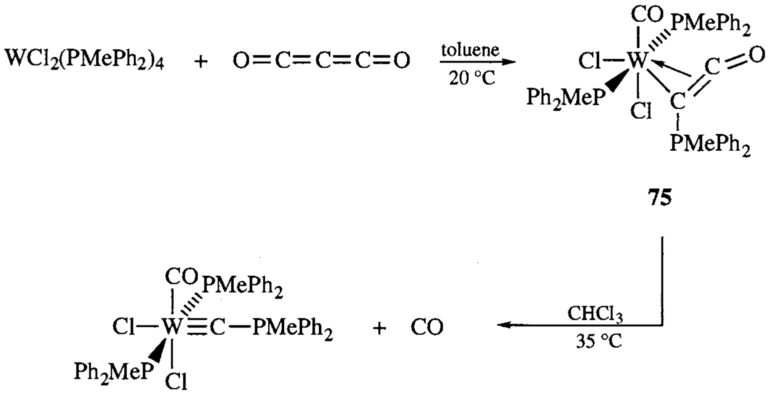
are not significantly influenced by the coordination to different metal centers. This is supported also by the reactivity of η^1-ketenyl ylidic complexes which react with nucleophiles.

The complex [Pt(η^3-C_3H_5)(PPh_3){η^1-C(PPh_3)CO}] reacts with Me_2NH giving the corresponding amidic derivative **80** (Eq. 42), which is formed as a mixture of two diasteroisomers due to the presence of a asymmetric carbon and the allyl group [70].

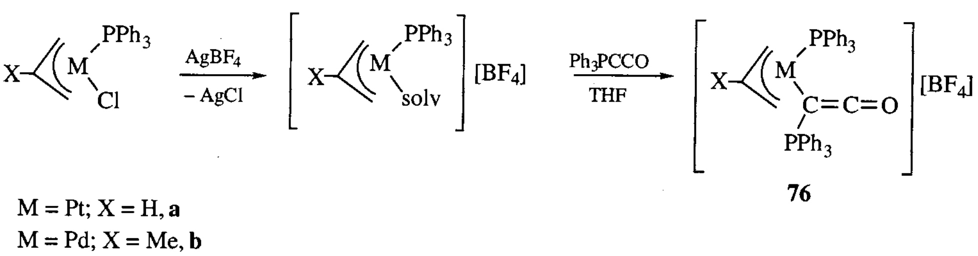


80

(42)

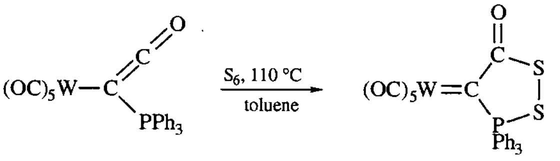


Scheme 19.



Scheme 20.

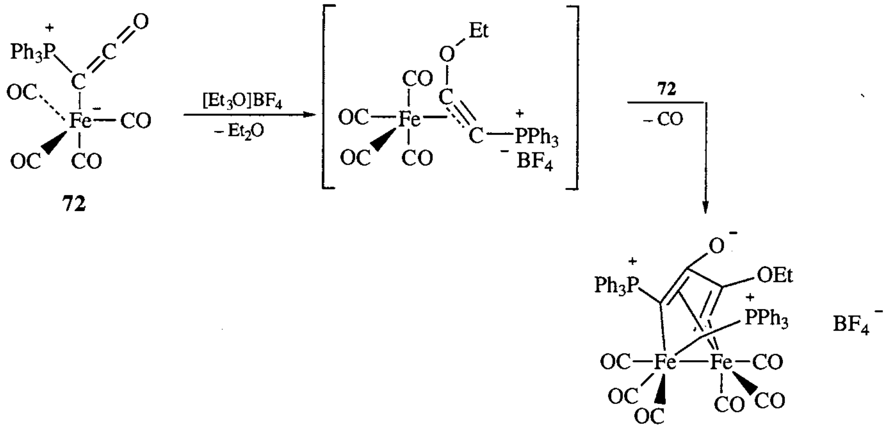
A peculiar reaction was reported in the literature between [W(CO)$_5${η^1-C(PPh$_3$)CO}] and sulfur [76] yielding a cyclic carbene derivative **81** (Eq. 43).



81

(43)

Furthermore [Fe(CO)$_4${η^1-C(PPh$_3$)CO}] is reported to react with [Et$_3$O][BF$_4$] [73] yielding the ionic compound **82** through a complex reaction (Eq. 44).

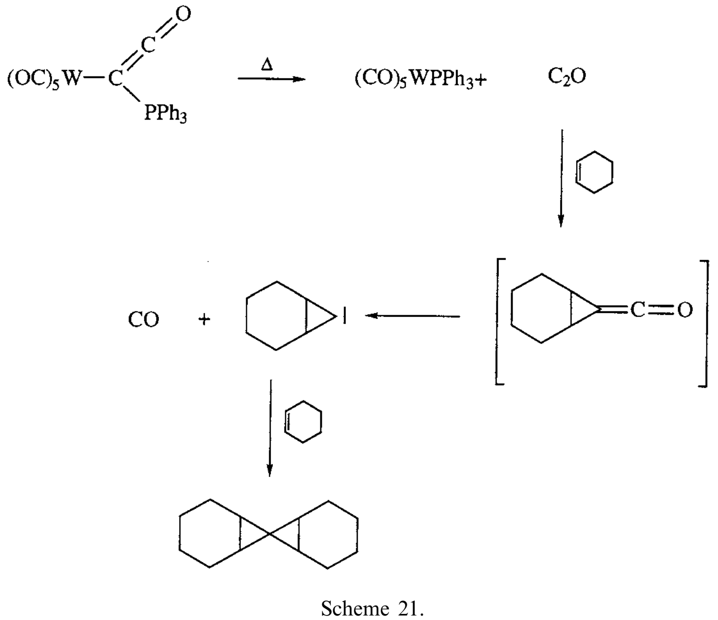


72

82

(44)

Finally, thermal decomposition of [M(CO)$_5${η^1-C(PPh$_3$)CO}] (M = Cr, Mo, W) yields [M(CO)$_5$(PPh$_3$)] whose formation results in the liberation of the carbonylmethylene unit CCO [72](a). In the case of tungsten complex, heating in the presence of a carbene trapping substance as cyclohexene, resulted in the formation of 7,7'-spirobinorcarane, according to Scheme 21. Reaction 38 and processes reported in Schemes 19 and 21 indicate that coordinated Ph$_3$PCCO can be useful synthon to 'C' and C$_1$ or C$_2$ organometallic fragments.



Scheme 21.

5. Conclusions

This review has described the progress to date in the area of functionalized ylide chemistry. Much of this work has focused on the synthesis, characterization and catalytic activity of their transition metal complexes. These ligands have been shown to be versatile reagents on which a rich metal- or ligand-centered chemistry can be based. It thus appears that the organometallic chemistry of functionalized ylides presents a challenge for further studies because of the variety of coordination modes presented by these ligands.

Acknowledgements

MURST and CNR are acknowledged for financial support. R.A.M. thanks CNR for a JNICT/CNR collaboration program. R.B. thanks CNR for the Progetto Strategico 'Tecnologie Chimiche Innovative'.

Appendix A. Abbreviations

Ylide	Formula	Abbreviation
Benzoylmethylenetriphenylphosphorane	$C_6H_5COCHP(C_6H_5)_3$	BPPY
Acetylmethylenetriphenylphosphorane	$CH_3COCHP(C_6H_5)_3$	APPY
Carbomethoxymethylenetriphenylphosphorane	$CH_3OCOCHP(C_6H_5)_3$	CMPPY
Benzoylmethylenetri-*n*-butylphosphorane	$C_6H_5COCHPBu_3$	BBuPY
Carbomethoxymethylenetriphenylarsenane	$CH_3OCOCHAs(C_6H_5)_3$	CMPAsY
Benzoylmethylenedimethylsulfurane	$C_6H_5COCHS(CH_3)_2$	BDMSY
Benzoylmethylenepyridinium ylid	$C_6H_5COCHNC_5H_5$	BPyY
Benzoylmethylenediphenyldiphenylphosphinomethylphosphorane	$Ph_2PCH_2PPh_2CHCOPh$	BDPDPPY
Acetylmethylenediphenyldiphenylphosphinomethylphosphorane	$Ph_2PCH_2PPh_2CHCOMe$	ADPPPY
Methoxybenzoylmethylenetricyclohexylphosphorane	C_6H_4-*p*-$OMeCOCHP(C_6H_5)_3$	BCyPYOMe
Acetylmethylenetriphenylarsorane	$CH_3COCHAs(C_6H_5)_3$	APAsY
Benzoylmethylenetriphenylarsorane	$PhCOCHAs(C_6H_5)_3$	BPAsY

References

[1] A.W. Johnson, Ylides and Imines of Phosphorus, John Wiley, New York, 1993.
[2] (a) H. Schmidbaur, Acc. Chem. Res. 8 (1975) 62. (b) H. Schmidbaur, Angew. Chem. Int. Ed. Engl. 22 (1983) 907.
[3] W.C. Kaska, Coord. Chem. Rev. 48 (1983) 1.
[4] L. Weber, in: F.R. Hartley, S. Patai (Eds.), The Chemistry of Metal–Carbon Bond, vol. 1, John Wiley, New York, 1982, p. 91.
[5] L.R. Falvello, S. Fernandez, R. Navarro, E.P. Urriolabeitia, Inorg. Chem. 35 (1996) 3064.
[6] (a) P.A. Arnup, M.C. Baird, Inorg. Nucl. Chem. Lett. 5 (1969) 65. (b) P.M. Maitlis, P. Espinet, M.J.H. Russel, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 6, Pergamon, New York, 1982, p. 299.
[7] G. Fronza, P. Bravo, C. Ticozzi, J. Organomet. Chem. 157 (1978) 299 and references therein.
[8] E.T. Weleski Jr., (The Late) J.L. Silver, M.D. Jansson, J.L. Burmeister, J. Organomet. Chem. 102 (1975) 365.
[9] P. Bravo, G. Fronza, C. Ticozzi, J. Organomet. Chem. 111 (1976) 361.
[10] H. Nishiyama, K. Itoh, Y. Ishii, J. Organomet. Chem. 87 (1975) 129.
[11] (a) M.L. Illingsworth, J.A. Teagle, J.L. Burmeister, W.C. Fultz, A.L. Rheingold, Organometallics 2 (1983) 1364. (b) J.A. Teagle, J.L. Burmeister, Inorg. Chim. Acta 118 (1986) 65. (c) J.A. Albanese, A.L. Rheingold, J.L. Burmeister, Inorg. Chim. Acta 150 (1988) 213.
[12] J.A. Albanese, D.L. Staley, A.L. Rheingold, J.L. Burmeister, J. Organomet. Chem. 375 (1989) 265.
[13] J. Vicente, M.T. Chicote, J. Fernandez-Baeza, J. Organomet. Chem. 364 (1989) 407.
[14] L.V. Rybin, E.A. Petrovskaya, M.I. Rybinskaya, L.G. Kuz'mina, Yu.T. Struchkov, V.V. Kaverin, N.Yu. Koneva, J. Organomet. Chem. 288 (1985) 119.
[15] H. Koezuka, G.-E. Matsubayashi, T. Tanaka, Inorg. Chem. 15 (1976) 417.
[16] M. Onishi, Y. Ohama, K. Hiraki, H. Shintani, Polyhedron 1 (1982) 539.

[17] (a) Y. Oosawa, T. Miyamoto, T. Saito, Y. Sasaki, Chem. Lett. (1975) 33. (b) Y. Oosawa, T. Saito, Y. Sasaki, Chem. Lett. (1975) 1259. (c) H. Takahashi, Y. Oosawa, A. Kobayashi, T. Saito, Y. Sasaki, Chem. Lett. (1976) 15. (d) H. Takahashi, Y. Oosawa, A. Kobayashi, T. Saito, Y. Sasaki, Bull. Chem. Soc. Jpn. 50 (1977) 1771. (e) Y. Oosawa, H. Urabe, T. Saito, Y. Sasaki, J. Organomet. Chem. 122 (1976) 113. (f) N. Sugita, T. Miyamoto, Y. Sasaki, Chem. Lett. (1976) 659.

[18] I.J.B. Lin, H.C. Shy, C.W. Liu, L.-K. Liu, S.-K. Yeh, J. Chem. Soc. Dalton Trans. (1990) 2509.

[19] R. Uson, J. Fornies, R. Navarro, A.M. Ortega, J. Organomet. Chem. 334 (1987) 389.

[20] G.-E. Matsubayashi, Y. Kondo, J. Organomet. Chem. 219 (1981) 269.

[21] (a) J. Vicente, M.-T. Chicote, J. Fernandez-Baeza, F.J. Lahoz, J.A. Lopez, Inorg. Chem. 30 (1991) 3617. (b) J. Vicente, M.T. Chicote, M.C. Lagunas, P.G. Jones, Inorg. Chem. 34 (1995) 5441.

[22] R.A. Michelin, M. Mozzon, R. Bertani, Coord. Chem. Rev. 147 (1996) 299.

[23] (a) J. Kiji, A. Matsumura, S. Okazaki, T. Haishi, J.Furukawa, J. Chem. Soc. Chem. Commun. (1975) 751. (b) P. Dapporto, G. Denti, G. Dolcetti, M. Ghedini, J. Chem. Soc. Dalton Trans. (1983) 779.

[24] J. Vicente, M.T. Chicote, M.A. Beswick, M.C. Ramirez de Arellano, Inorg. Chem. 35 (1996) 6592.

[25] R.A. Wanat, D.B. Collum, Organometallics 5 (1986) 120.

[26] E. Carmona, E. Gutiérrez-Puebla, A. Monge, J.M. Marin, M. Paneque, M.L. Poveda, Organometallics 3 (1984) 1438.

[27] H.G. Alt, U. Thewalt, J. Organomet. Chem. 268 (1984) 235.

[28] (a) J. Vicente, M.-T. Chicote, M.-C. Lagunas, P.G. Jones, J. Chem. Soc. Dalton Trans. (1991) 2579. (b) J. Vicente, M.T. Chicote, J.A. Cayuelas, J. Fernandez-Baeza, P.G. Jones, G.M. Sheldrick, P. Espinet, J. Chem. Soc. Dalton Trans. (1985) 1163. (c) J. Vicente, M.T. Chicote, J. Fernandez-Baeza, J. Martin, I. Saura-Llamas, J. Turpin, P.G. Jones, J. Organomet. Chem. 331 (1987) 409. (d) J. Vicente, M.T. Chicote, I. Saura-Llamas, J. Turpin, J. Fernandez-Baeza, J. Organomet. Chem. 333 (1987) 129. (e) J. Vicente, M.T. Chicote, I. Saura-Llamas, P.G. Jones, K.M. Base, C.F. Erdbrugger, Organometallics 7 (1988) 997.

[29] P. Lennon, A.M. Rosan, M. Rosenblum, J. Am. Chem. Soc. 99 (1977) 8426.

[30] S. Voran, W. Malisch, Angew. Chem. Int. Ed. Engl. 22 (1983) 151.

[31] M. Kalyanasundari, K. Panchanatheswaran, W.T. Robinson, H. Wen, J. Organomet. Chem. 491 (1995) 103.

[32] T. Saito, Bull. Chem. Soc. Jpn. 51 (1978) 169.

[33] (a) J. Buckle, P.G. Harrison, T.J. King, J.A. Richards, J. Chem. Soc. Chem. Commun. (1972) 1104. (b) P.G. Harrison, T.J. King, J. Chem. Soc. Chem. Commun. (1972) 815.

[34] (a) J. Buckle, P.G. Harrison, J. Organomet. Chem. 49 (1973) C17. (b) S. Kato, T. Kato, M. Mizuta, K. Itoh, Y. Ishii, J. Organomet. Chem. 51 (1973) 167.

[35] I. Kawafune, G.-E. Matsubayashi, Inorg. Chim. Acta 70 (1983) 1.

[36] J.A. Albanese, D.L. Staley, A.L. Rheingold, J.L. Burmeister, Inorg. Chem. 29 (1990) 2209.

[37] R. Uson, J. Fornies, R. Navarro, P. Espinet, C. Mendivil, J. Organomet. Chem. 290 (1985) 125.

[38] G. Erker, U. Korek, R. Schlund, C. Kruger, J. Organomet. Chem. 364 (1989) 133.

[39] A.J. Deeming, D. Nuel, N.I. Powell, C. Whittaker, J. Chem. Soc. Dalton Trans. (1992) 757.

[40] U. Belluco, R.A. Michelin, R. Bertani, G. Facchin, G. Pace, L. Zanotto, M. Mozzon, M. Furlan, E. Zangrando, Inorg. Chim. Acta 252 (1996) 355.

[41] G. Facchin, R. Bertani, M. Calligaris, G. Nardin, M. Mari, J. Chem. Soc. Dalton Trans. (1987) 1381.

[42] P. Uguagliati, L. Canovese, G. Facchin, L. Zanotto, Inorg. Chim. Acta 192 (1992) 283.

[43] (a) A.J. Speziale, K.W. Ratts, J. Am. Chem. Soc. 85 (1963) 2790. (b) G. Askens, J. Songstad, Acta Scand. 18 (1964) 655. (c) S. Fliszar, R.F. Hudson, G. Salvadori, Helv. Chim. Acta 46 (1963) 1580. (d) A.W. Johnson, R.T. Amel, Can. J. Chem. 46 (1968) 461.

[44] G. Facchin, R. Bertani, L. Zanotto, M. Calligaris, G. Nardin, J. Organomet. Chem. 366 (1989) 409.

[45] G. Facchin, L. Zanotto, R. Bertani, G. Nardin, Inorg.Chim.Acta 245 (1996) 157.

[46] (a) M.A.M. Meester, D.J. Stufkens, K. Vrieze, Inorg. Chim. Acta 14 (1975) 25; (b) idem, ibidem 16 (1976) 191. (c) idem, ibidem 21 (1977) 251. (d) T.G. Appleton, H.C. Clark, L.E. Manzer, Coord. Chem. Rev. 10 (1973) 335. (e) P.S. Pregosin, S.N. Sze, P. Salvadori, R. Lazzaroni, Helv. Chim. Acta 60 (1977) 2514.

[47] (a) A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, J. Chem. Soc. Dalton Trans. (1989) S1. (b) G. Strukul, R.A. Michelin, J.D. Orbell, L. Randaccio, Inorg. Chem. 22 (1983) 3706.

[48] G. Facchin, L. Zanotto, R. Bertani, L. Canovese, P. Uguagliati, J. Chem. Soc. Dalton Trans. (1993) 2871.

[49] E. Drent, J.A.M. van Broekhoven, P.H.M. Budzelaar, in: B. Cornil, W.A. Hermann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1, VCH, Weinheim, 1996, p. 333.

[50] (a) W. Keim, F.H. Howaldt, R. Goddard, C. Kruger, Angew. Chem. Int. Ed. Engl. 17 (1978) 466. (b) W. Keim, A. Behr, B. Limbaker, C. Kruger, Angew. Chem. Int. Ed. Engl. 22 (1983) 503. (c) A. Behr, W. Keim, G. Thelen, J. Organomet. Chem. 249 (1993) C38; (d) V.M. Mohring, G. Fink, Angew. Int. Ed. Engl. 24 (1985) 1001.

[51] (a) D. Vogt, in: B. Cornil, W.A. Hermann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1, VCH, Weinheim, 1996, p. 245. (b) U. Klabunde, T.H. Tulip, D.C. Roe, S.D. Ittel, J. Organomet. Chem., 334 (1987) 141. (c) U. Klabunde, S.D. Ittel, J. Mol. Cat. 41 (1987) 123.

[52] M. Peuckert, W. Keim, J. Mol. Catal. 22 (1984) 289.

[53] (a) K.A.O. Starzewski, J. Witte, Angew. Chem., Int. Ed. Engl. 24 (1985) 599. (b) K.A. O. Starzewski, J. Witte, Angew. Chem., Int. Ed. Engl. 26 (1987) 63. (c) Idem, Angew. Chem., Int. Ed. Engl. 27 (1988) 839. (d) K.A.O. Starzewski, G.M. Bayer, Angew. Chem. Int. Ed. Engl. 30 (1991) 961.

[54] K.A.O. Starzewski, L. Born, Organometallics 11 (1992) 2701.

[55] W. Keim, A. Behr, B. Gruber, B. Hoffmann, F.H. Kowaldt, U. Kurschner, B. Limbaker, F.P. Sistig, Organometallics 5 (1986) 2356.

[56] R.A. Michelin, G. Facchin, D. Braga, P. Sabatino, Organometallics 5 (1986) 2265.

[57] E.M. Badley, J. Chatt, R.L. Richards, J. Chem. Soc. A, (1971) 21.

[58] B. Crociani, T. Boschi, U. Belluco, Inorg. Chem. 9 (1970) 2021.

[59] U. Belluco, R.A. Michelin, P. Uguagliati, B. Crociani, J. Organomet. Chem. 250 (1983) 565.

[60] U. Schubert, Transition Metal Carbene Complexes, VCH, Weinheim, 1983, p. 73.

[61] S. Voran, H. Blaw, W. Malish, U. Schubert, J. Organomet. Chem. 232 (1982) C33.
[62] N.E. Kolobova, L.L. Ivanov, O.S. Zhvanko, I.N. Chechulina, A.S. Batsanov, Y.J. Strukov, J. Organomet. Chem. 238 (1983) 223.
[63] W. Malisch, H. Blaw, U. Schubert, Chem. Ber. 116 (1983) 690.
[64] D. Barton, W.D. Ollis, in: P.G. Sammer (Ed.), Comprehensive Organic Chemistry, vol. 4, Pergamon Press, Oxford, 1979, p. 411.
[65] R.A. Michelin, M. Mozzon, G. Facchin, D. Braga, P. Sabatino, J. Chem. Soc. Dalton Trans. (1988) 1803.
[66] G. Facchin, M. Mozzon, R.A. Michelin, M.T.A. Ribeiro, A.J.L. Pombeiro, J. Chem. Soc. Dalton Trans. (1992) 2827.
[67] G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 3, Pergamon Press, Oxford, 1982.
[68] H.J. Bestmann, Angew. Chem. Int. Ed. Engl. 16 (1977) 349.
[69] (a) C.M. Matthews, G.H. Birum, Tetrahedron Lett. 46 (1966) 5707. (b) J.J. Daly, P.J. Wheatley, J. Chem. Soc. (A) (1966) 1703. (c) H.J. Bestmann, D. Sandmeier, Chem. Ber. 113 (1980) 274.
[70] (a) G.L. Geoffroy, S.L. Bassner, Adv. Organomet. Chem. 28 (1988) 1. (b) F. Calderazzo, U. Englert, A. Guarini, F. Marchetti, G. Pampaloni, A. Segre, G. Tripepi, Chem. Eur. J. 2 (1996) 412. (c) W.A. Herrmann, Angew. Chem. Int. Ed. Engl. 21 (1982) 117.
[71] L. Pandolfo, G. Paiaro, L.K. Dragani, C. Maccato, R. Bertani, G. Facchin, L. Zanotto, P. Ganis, G. Valle, Organometallics 15 (1996) 3250.
[72] (a) H. Berke, E. Lindner, Angew. Chem. Int. Ed. Engl. 12 (1973) 667. (b) E. Lindner, J. Organomet. Chem. 94 (1975) 229.
[73] H. Lindenberger, R. Birk, O. Orama, G. Hutter, H. Berke, Z. Naturforsh. 43b (1988) 749.
[74] A.K. List, G. Hillhouse, A.L. Rheingold, Organometallics 8 (1989) 2010.
[75] R. Bertani, L. Pandolfo et al., unpublished results.
[76] E. Lindner, J. Organomet. Chem. 94 (1975) 229.
[77] N.A. Nesmeyanov, V.V. Mikulshina, O.A. Reutov, J. Organomet. Chem. 13 (1968) 263.