Synthesis of New Phosphonium Ylides Containing Thiophene and Furan Rings and Study of Their Reaction with Mercury(II) Halides: Spectral and Structural Characterization

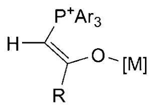
by **Seyyed Javad Sabounchei***[a]), **Vida Jodaian**[b]), **Sadegh Salehzadeh**[a]), **Sepideh Samiee**[a]), **Alireza Dadrass**[a]), **Mehdi Bayat**[a]), and **Hamid Reza Khavasi**[c])

[a]) Faculty of Chemistry, Bu-Ali Sina University, Hamedan, 65174, Iran
(phone: +98-811-8282807; fax: +98-811-8257407; e-mail: jsabounchei@yahoo.co.uk)
[b]) Islamic Azad University, Islamshahr Branch 33135/369
[c]) Department of Chemistry, Shahid Beheshti University, Evin, Tehran, 19839-63113, Iran

---

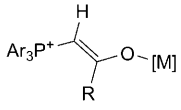
Reactions of phosphonium ylides $(4\text{-MeC}_6H_4)_3PCHC(=O)(2\text{-C}_4H_3S)$ (tptpy), $Ph_3PCHC(=O)(2\text{-C}_4H_3O)$ (fppy), and $(4\text{-MeC}_6H_4)_3PCHC(=O)(4\text{-BrC}_6H_4)$ (bbtppy) with HgX_2 (X = Cl, Br, and I) in equimolar ratios in MeOH as solvent leads to the binuclear products **1**–**3** (*Scheme 1*). The bridge-splitting reaction of the binuclear complex $[\{HgI_2(\text{bbtppy})\}_2]$ (**3c**) by DMSO yields the mononuclear complex $[HgI_2 \cdot (\text{bbtppy})(\text{DMSO})]$ (**3d**) (*Scheme 2*). This bridge-splitting reaction can also be a method for the synthesis of mononuclear products. *C*-Coordination of the ylide and *O*-coordination of DMSO are demonstrated by a single-crystal X-ray-analysis of the mononuclear complex **3d**. Characterization of the obtained compounds was also performed by means of elemental analysis and IR and ^1H-, ^{31}P-, and ^{13}C-NMR spectroscopy. A theoretical study of some Hg^{II} complexes with phosphonium ylides is also reported.

Introduction. – The coordination chemistry of the phosphonium ylides (= phosphoranes) of the type $R_3P^+-CH_2^-$, is well known [1–4]. Resonance-stabilized phosphonium ylides, particularly, the keto ylides, are also successfully used as ligands in organometallic and coordination chemistry owing to their accessibility and stability towards air and moisture [5][6]. Juxtaposition of the keto group and the carbanion in the phosphonium ylides allows for the resonance delocalization of the ylide electron density providing additional stabilization to the ylide species. This so-called α-stabilization provides ylides with the potential to act as an ambidentate ligand and thus bond to an Hg^{II} center through either the C-atom (see **B**) or O-atom (see $\mathbf{A_1}$ and $\mathbf{A_2}$).



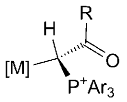
$\mathbf{A_1}$

O-Coordination, *cisoid*



$\mathbf{A_2}$

O-Coordination, *transoid*



B

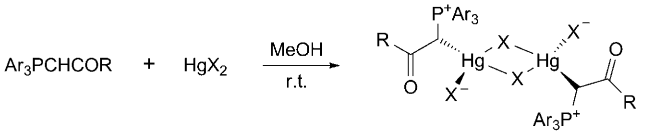
C-Coordination

Although many bonding modes are possible for keto ylides [7], coordination through the C-atom is more predominant and observed with soft metal ions, *e.g.*, Pd^{II}, Pt^{II}, Ag^{I}, Hg^{II}, Au^{I}, and Au^{III} [8][9–12], whereas *O*-coordination dominates when the metals involved are hard, *e.g.*, Ti^{IV}, Zr^{IV}, and Hf^{IV} [13].

The investigation of the reactivity and coordination chemistry of C=O-group-stabilized ylides is the research field of our group. We were interested in the synthesis of new types of phosphonium ylides containing thienyl or furanyl groups and the study of their interaction with Hg^{II} halides.

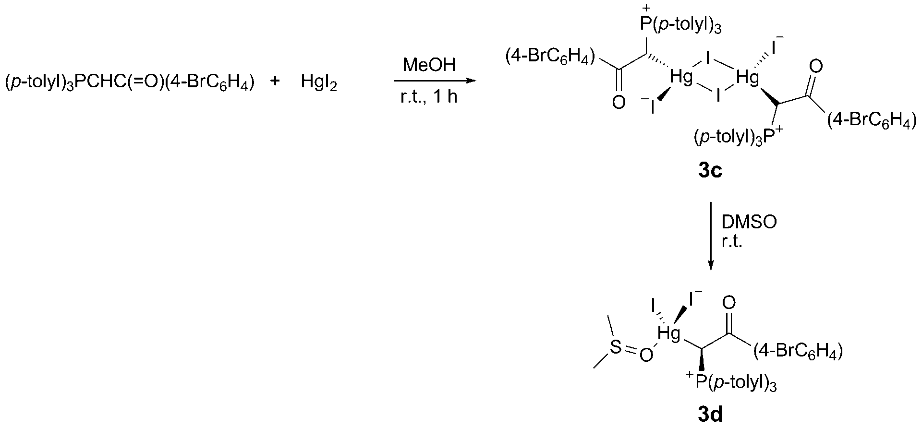
Results and Discussion. – *Spectroscopy.* The $\tilde{\nu}_{C=O}$ of the phosphonium ylide ligands, which is sensitive to complexation to Hg^{II}, occurs at higher frequencies in the complexes **1**–**3** (see *Schemes 1* and *2*) as compared to the parent ylides, indicating coordination of the ylides through their C-atom (*Table 1*). *C*-Coordination causes an increase in $\tilde{\nu}_{C=O}$, but for *O*-coordination, a lowering is expected. The $\tilde{\nu}_{P^+-C^-}$, which is also diagnostic for the coordination, occurs at lower frequencies for the complexes, suggesting some lowering of the electron density of the P–C bond [14][15] (*Table 1*).

Scheme 1



	R	Ar	X
1a	thien-2-yl	4-MeC$_6$H$_4$	Cl
1b	thien-2-yl	4-MeC$_6$H$_4$	Br
1c	thien-2-yl	4-MeC$_6$H$_4$	I
2a	furan-2-yl	Ph	Cl
2b	furan-2-yl	Ph	Br
2c	furan-2-yl	Ph	I
3a	4-BrC$_6$H$_4$	4-MeC$_6$H$_4$	Cl
3b	4-BrC$_6$H$_4$	4-MeC$_6$H$_4$	Br
3c	4-BrC$_6$H$_4$	4-MeC$_6$H$_4$	I

Scheme 2



The ^1H- and ^{31}P-NMR data for the Hg^{II} complexes, along with those of the parent ylides, are listed in *Table 2*. The expected downfield shifts of the ^{31}P and ^1H signals of

Table 1. *Assignment of Characteristic FT-IR Vibrations of Ligands and Their Hg^{II} Halide Complexes*

	$\tilde{\nu}_{C=O}$ [cm^{-1}]	$\nu_{P^+-C^-}$ [cm^{-1}]	Ref.
$Ph_3PCHC(=O)(4\text{-}MeOC_6H_4)$ (mbppy)	1521	884	[16]
$(4\text{-}MeC_6H_4)_3PCHCO_2CH_2Ph$ (btpy)	1615	811	[17]
$(4\text{-}MeC_6H_4)_3PCHC(=O)(2\text{-}C_4H_3S)$ (tptpy)	1524	927	a)
1a	1613	808	a)
1b	1618	804	a)
1c	1609	803	a)
$Ph_3PCHC(=O)(2\text{-}C_4H_3O)$ (fppy)	1526	874	a)
2a	1633	811	a)
2b	1624	810	a)
2c	1625	811	a)
$(4\text{-}MeC_6H_4)_3PCHC(=O)(4\text{-}BrC_6H_4)$ (bbtppy)	1598	882	a)
3a	1646	805	a)
3b	1635	804	a)
3c	1641	800	a)
3d	1640	797	a)
$[\{HgCl_2(mbppy)\}_2]$	1630	825	[16]
$[\{HgBr_2(mbppy)\}_2]$	1626	820	[16]
$[\{HgI_2(mbppy)\}_2]$	1620	812	[16]
$[\{HgCl_2(btpy)\}_2]_2$	1702	805	[17]
$[\{HgBr_2(btpy)\}_2]_2$	1699	806	[17]

a) This work.

Table 2. *^{31}P- and ^{1}H-NMR Data of Ligands and Their Hg^{II} Halide Complexes.* δ in ppm.

	$^{31}P\{^1H\}$-NMR a)	CH a)	Ref.
$Ph_3PCHC(=O)(4\text{-}MeOC_6H_4)$ (mbppy)	14.06 (*s*)	4.25 (*d*)	[16]
$(4\text{-}MeC_6H_4)_3PCHCO_2CH_2Ph$ (btpy)	13.90 (*s*)	2.88 (*d*)	[17]
$(4\text{-}MeC_6H_4)_3PCH(=O)(2\text{-}C_4H_3S)$ (tptpy) b)	12.63 (*s*)	4.24 (br.)	c)
1a d)	23.74 (*s*)	5.36 (*d*)	c)
1b d)	23.63 (*s*)	5.30 (*d*)	c)
1c d)	22.42 (*s*)	5.29 (*d*)	c)
$Ph_3PCH(=O)(2\text{-}C_4H_3O)$ (fppy) b)	13.69 (*s*)	4.17 (br.)	c)
2a d)	20.00 (*s*)	5.06 (br.)	c)
2b d)	22.28 (*s*)	5.15 (br.)	c)
2c d)	21.88 (*s*)	5.24 (br.)	c)
$(4\text{-}MeC_6H_4)_3PCHC(=O)(4\text{-}BrC_6H_4)$ (bbtppy) b)	13.28 (*s*)	4.43 (*d*)	c)
3a d)	23.45 (*s*)	5.30 (br.)	c)
3b d)	22.14 (*s*)	5.30 (*d*)	c)
3c d)	21.72 (*s*)	5.53 (br.)	c)
3d d)	21.57 (*s*)	5.43 (br.)	c)
$[\{HgCl_2(mbppy)\}_2]$	24.58 (*s*)	5.43 (*d*)	[16]
$[\{HgBr_2(mbppy)\}_2]$	23.58 (*s*)	5.45 (*d*)	[16]
$[\{HgCl_2(btpy)\}_2]$	23.85 (*s*)	4.25 (br.)	[17]

a) At *T* 298 K; chemical shifts in ppm relative to internal Me_4Si (= 0.00 ppm) and external 85% H_3PO_4. b) In $CDCl_3$. c) This work. d) In (D_6)DMSO.

the PCH group upon complexation are observed with respect to the free ylides in the corresponding spectra. The appearance of single signals for the PCH group, in both the ^{31}P- and ^{1}H-NMR spectra at room temperature, indicates the presence of only one molecule for all complexes, as expected for *C*-coordination. It must be noted that *O*-coordination of the ylide leads to the formation of a *cisoid* and a *transoid* isomer giving rise to two different signals in the ^{31}P- and ^{1}H-NMR spectra [13]. Moreover, there is no significant difference in the data reported for the binuclear **3c** and the related mononuclear complex **3d**.

The ^{13}C-NMR data of the complexes and the title ylides along with possible assignments are listed in *Tables 3–5*. The ^{13}C-NMR shifts of the C=O group in the complexes are around δ 170, *i.e.*, at lower field than for the free phosphonium ylides, indicating a much lower shielding of the C-atom of the C=O group in the complexes.

Table 3. *^{13}C-NMR Data of $(4\text{-MeC}_6H_4)_3PCH(=O)(2\text{-}C_4H_3S)$* (tptpy) *and Its Complexes with Hg^{II} Halides*

	tptpy a)	[{HgCl$_2$(tptpy)}$_2$] (**1a**) b)	[{HgBr$_2$(tptpy)}$_2$] (**1b**) b)	[{HgI$_2$(tptpy)}$_2$] (**1c**) b)
CH	50.67	(br.)	(br.)	(br.)
^{1}J(P,C)	112.82	–	–	–
C(2,6) c)	132.47	133.1	133.04	133.39
^{2}J(P,C)	10.27	10.49	10.67	10.49
C(3,5) c)	128.99	129.91	129.88	130.39
^{3}J(P,C)	12.50	12.86	13.02	12.86
C(4) c)	126.27	132.22	132.81	133.62
^{4}J(P,C)	5.47	–	–	–
C(1) c)	123.12	119.79	119.76	119.81
^{1}J(P,C)	92.41	91.68	93.55	100.88
Me c)	20.81	20.95	20.95	21.37
C_4H_3S	123.12, 125.29, 141.95, 148.35	128.06, 143.97, 144.64 (2:1:1)	128.02, 144.04, 144.05 (2:1:1)	128.60, 133.6, 144.67 (2:1:1)
C=O	177.33	183.97	183.68	183.83

a) In $CDCl_3$. b) In (D_6)DMSO. c) C-Atoms of $P(4\text{-MeC}_6H_4)_3$.

No coupling to Hg is observed at room temperature in the ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra. Failure to observe satellites in the above spectra was previously noted for the ylide complexes of Hg^{II} [14] and Ag^{I} [11] which had been explained by fast exchange of the ylide with the metal.

Crystal-Structure Analysis of **3d**. *Table 6* provides the crystallographic results and refinements for complex **3d**. The molecular structure is shown in *Fig. 1*, and selected bond distances and angles are given in *Table 7*.

The Hg^{II} center of complex **3d** is coordinated by one C-, one O-, and two I-atoms in a distorted tetrahedral geometry. The two different Hg–I distances of **3d** (2.6776(8) and 2.7130(8) Å) are smaller than those found in the mononuclear complex [HgI$_2$(PPh$_3$)$_2$] (2.733(1) and 2.763(1) Å) [16] indicating relatively strong Hg–I bonds in **3d**. The above distances are comparable to the Hg–I distances of 2.693(2) and 2.727(2) Å found in [HgI$_2${Ph$_2$P(S)CH$_2$PPh$_2$}] [18] and to the terminal Hg–I distance of 2.6999(6) Å reported for the dimeric complex [{HgI$_2${(4-MeC$_6$H$_4$)$_3$PCHC(=O)(4-

Table 4. *^{13}C-NMR Data of $P_3PCH(=O)(2-C_4H_3O)$* (fppy) *and Its Complexes with Hg^{II} Halides*

	fppy^a)	[{HgCl$_2$(fppy)}$_2$] (**2a**)^b)	[{HgBr$_2$(fppy)}$_2$] (**2b**)^b)	[{HgI$_2$(fppy)}$_2$] (**2c**)^b)
CH	50.11	46.32	47.13	(br.)
^1J(P,C)	113.58	72.06	70.42	–
C(2,6)^c)	132.9	133.21	133.27	133.2
^2J(P,C)	10.20	10.00	10.52	9.91
C(3,5)^c)	128.61	129.39	129.53	129.56
^3J(P,C)	12.23	12.32	12.39	12.32
C(4)^c)	131.92	133.43	133.5	133.42
^4J(P,C)	2.53	–	–	–
C(1)^c)	126.39	123.39	123.15	123.24
^1J(P,C)	91.35	89.72	89.81	89.84
C_4H_3O	109.08, 110.97, 141.99, 155.81	112.09, 115.81, 145.90, 152.18	112.37, 116.33, 146.37, 152.13	112.49, 117.01, 146.54, 151.61
C=O	174.88	178.8	179.03	179.41

^{a}) In CDCl$_3$. ^{b}) In (D$_6$)DMSO. ^{c}) C-Atoms of PPh$_3$.

Table 5. *^{13}C-NMR Data of $(4-MeC_6H_4)_3PCHC(=O)(4-BrC_6H_4)$* (bbtppy) *and Its Complexes with Hg^{II} Halides*

	bbtppy^a)	[{HgCl$_2$(bbtppy)}$_2$] (**3a**)^b)	[{HgBr$_2$(bbtppy)}$_2$] (**3b**)^b)	[{HgI$_2$(bbtppy)}$_2$] (**3c**)^b)
CH	51.46 (*d*)	(br.)	(br.)	(br.)
^1J(P,C)	107.12	–	–	–
Me^c)	21.52	20.87	21.04	21.72
C(2,6)^c)	133.13	133.02	133.17	133.02
^2J(P,C)	10.58	10.58	10.13	9.05
C(3,5)^c)	129.66	129.47	129.97	129.47
^3J(P,C)	12.84	12.61	11.93	12.82
C(4)^c)	130.73	130.76	130.92	130.76
C(1)^c)	126.12	127.76	128	129.17
^1J(P,C)	118.27	101.82	99.12	89.01
4-BrC$_6$H$_4$	142.71, 128.75, 121.9, 123.44	143.74, 130.05, 122.37, 118.32	143.89, 132.57, 122.47, 118.34	144.86, 136.58, 120.72, 119.48
C=O	183.11	188.73	189.17	191.48

^{a}) In CDCl$_3$. ^{b}) In (D$_6$)DMSO. ^{c}) C-Atoms of P(4-MeC$_6$H$_4$)$_3$.

ClC$_6$H$_4$)}}$_2$] [19]. The difference between the two distances in these complexes might be arising from steric effects of the large ylide moieties.

The Hg–I(1), Hg–I(2), and Hg–C bond lengths of **3d** (2.6776(8), 2.7130(8), and 2.261(7) Å, resp.) are shorter than those found in the binuclear complex [{HgI$_2${(4-MeC$_6$H$_4$)$_3$PCHC(=O)(4-ClC$_6$H$_4$)}}$_2$ (2.699(6), 2.7902(5), and 2.310(6) Å, resp.) indicating relatively strong bonds in the mononuclear complexes compared to the binuclear complexes [19].

The *C*-coordination of the title ylides is in contrast to the *O*-coordination of the phosphonium ylide Ph$_3$PC(COMe)(COPh) (abppy) in a different Hg^{II} complex [20].

Table 6. *Crystallographic Data of Compound* **3d**

Identification code	119 kh
Empirical formula	$C_{31}H_{32}BrHgI_2O_2PS$
M_r	1033.90
Crystal demensions [mm]	0.30 × 0.20 × 0.20
Temperature [K]	293(2)
Crystal system	monoclinic
Space group	$P2(1)/n$
Z	4
Unit cell parameters:	
a [Å]	11.644(10)
b [Å]	14.4249(17)
c [Å]	21.2686(17)
β [°]	104.223(6)
V [Å^3]	3462.9(6)
Absorption coefficient [mm^{-1}]	7.513
$F(000)$	1944
θ Range for data collection [°]	1.72–26.88
Limiting indices	$-14 \leq h \leq 14$; $-18 \leq k \leq 18$; $-26 \leq l \leq 26$
Reflections collected, unique	35267, 7355 (R(int) = 0.1113)
Completeness to $\theta = 26.80$	98.5%
Absorption correction	numerical
Max. and min. transmission	0.985; 0.620
Refinement method	full-matrix least-squares on F^2
Data, restraints, parameters	7355, 0, 354
Goodness-of-fit on F^2	1.167
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0575$, $wR_2 = 0.1348$
R Indices (all data)	$R_1 = 0.0704$, $wR_2 = 0.1417$
Largest diff. peak and hole [e Å^3]	1.538; -1.396

Table 7. *Selected Bond Lengths and Bond Angles of* **3d**[a])

	Bond lengths [Å]		Bond angles [°]
Hg(1)–I(1)	2.6776(8)	C(1)–Hg(1)–I(1)	119.33(17)
Hg(1)–I(2)	2.7130(8)	C(1)–Hg(1)–I(2)	121.38(17)
Hg(1)–C(1)	2.261(7)	I(1)–Hg(1)–I(2)	117.38(3)
P(1)–C(23)	1.791(8)	O(2)–Hg(1)–I(1)	101.94(17)
P(1)–C(1)	1.799(7)	O(2)–Hg(1)–I(2)	97.95(17)
P(1)–C(9)	1.806(7)	C(1)–Hg(1)–O(2)	84.1(2)
P(1)–C(16))	1.797(8)	C(2)–C(1)–P(1)	113.5(5)
O(2)–S(1)	1.496(7)	C(2)–C(1)–Hg(1)	107.3(5)
		P(1)–C(1)–Hg(1)	110.2(3)
		C(23)–P(1)–C(16)	109.6(4)

[a]) See *Fig. 1* for the atom numbering.

The difference in the coordination mode of abppy and of the present ylides to Hg^{II} can be rationalized in terms of the electronic properties, steric requirements, size, and shape of the ligand in the final bonding mode. This may also be explained by the electronic nature of the metal (Pd, Pt, Ru, Au, *etc.*) and even the position of the coordination site

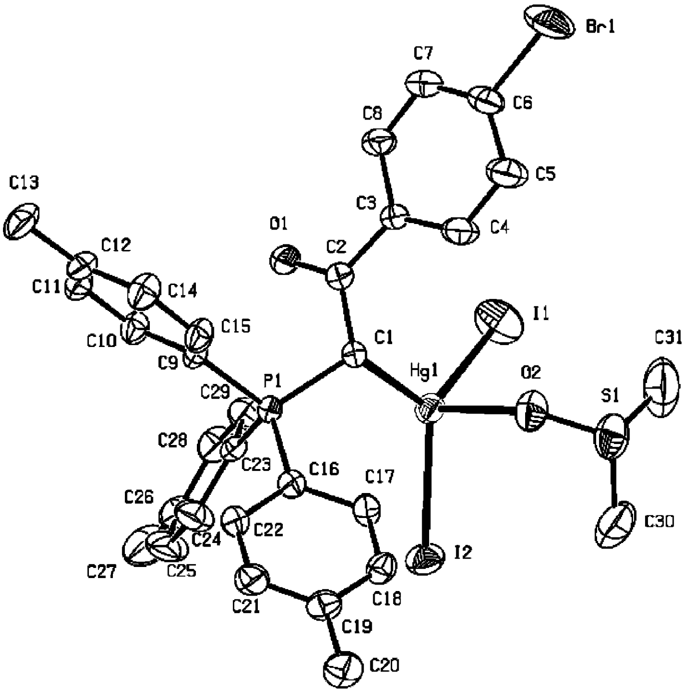


Fig. 1. *ORTEP View of the X-ray crystal structure of [HgI$_2$(bbtppy)(DMSO)]* (**3d**). Arbitrary atom numbering.

(*trans* to a C-, N-, or O-atom, *etc.*). The nucleophilicity of the carbanion in abppy is smaller than in our ylides; this is due to the additional delocalization of the ylide electron density in abppy which is facilitated by the second C=O group. This will reduce the ability of abppy to form bonds *via* the ylide C-atom. *Facchin* and co-workers have studied the steric influences on the coordination modes of ylide molecules to Pt^{II} systems [21]. These authors concluded that the preferred coordination takes place *via* the ylide C-atom, but that steric hindrance around the metal center or the ylide C-atom will favor *O*-coordination. Indeed, this trend is reflected here, our ylides are sterically slightly less demanding than abppy and are *C*-coordinated to Hg^{II}.

Literature data show that the coordination mode of dimethyl sulfoxide (=sulfinylbis[methane]=DMSO) to relatively soft metal atoms depends on both electronic and steric factors originating from the moderate π-acceptor properties of DMSO and its greater steric demand in the case of *S*-bonding [22]. In the case of Ru^{II} complexes, coordination through the S-atom of DMSO seems to be preferred over coordination through the O-atom of DMSO to get stable species, unless ligand overcrowding occurs [23] or DMSO is *trans*-oriented to strong π-acceptors like C=O [24] and NO [25][26]. A similar overestimate is found for the calculated S–O distance in 'free' DMSO (1.509 Å), which is 0.018 Å longer than the experimental reference value of 1.492(1) Å [27]. The significant elongation of the S–O distance upon *O*-coordination is further confirmed by the recent X-ray structure analysis of a disulfoxide and related Cu^{II} complexes, where the average S–O distances are 1.487(4) Å (free) and 1.520(3) Å (*O*-bonded) [28]. The present work reports the example of a Hg^{II} complex containing DMSO as ligand with an *O*-coordination mode. It is worth noting that in **3d**, the S–O bond distance of 1.496(7) Å is *ca.* 0.004 Å longer than the experimental reference value of 1.492(1) Å for the free DMSO ligand [27].

Theoretical Studies. As discussed in the previous section, the mononuclear complex **3d** is formed by the reaction of complex **3c** with DMSO. Recently, according to a theoretical gas-phase study with only a LanL2MB basis set, we showed that such a reaction is *ca.* 32–40 kcal/mol exothermic for a number of Hg^{II} complexes [19]. Thus, we became interested to know whether and to what an extent the formation of mononuclear complexes in the gas phase in which DMSO acts as ligand is energetically favored over that of binuclear complexes containing the ylide bbtppy. The structures of the mononuclear complexes derived from the reaction of compounds **3a**–**3c** with DMSO were optimized with the LanL2MB and LanL2DZ basis sets. The LanL2DZ-optimized structures are shown in *Fig. 2*. A comparison between the calculated bond lengths and bond angles of **3d** obtained with the LanL2MB and LanL2DZ basis sets

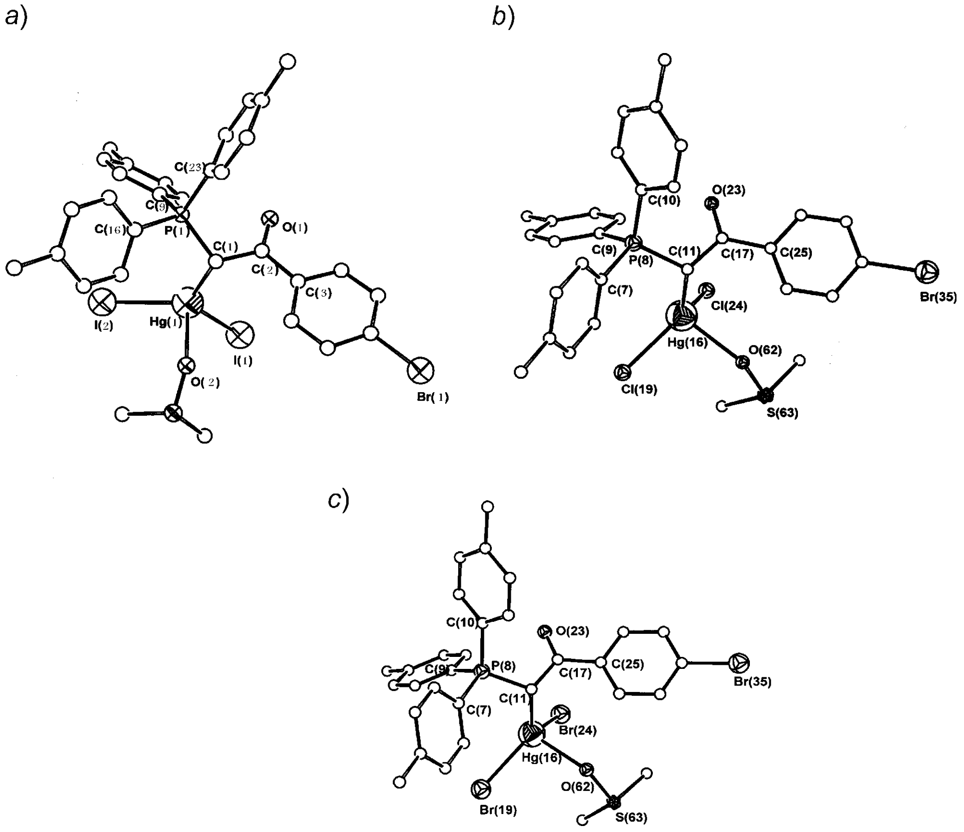


Fig. 2. *Calculated molecular structures of* a) *[HgI_2(bbtppy)(DMSO)],* b) *[$HgBr_2$(bbtppy)(DMSO)], and* c) *[$HgCl_2$(bbtppy)(DMSO)].* Arbitrary atom numbering.

with corresponding experimental values is presented in *Table 8*. A list of calculated key bond lengths and bond angles for compounds $[HgX_2(bbtppy)(DMSO)]$ (where X = Cl and Br) are also presented in *Table 9*.

As can be seen, the data derived from the more expensive basis set LanL2DZ are much closer to the experimental data of **3d** than those derived from the cheaper basis set LanL2MB. As can be seen, in the case of the LanL2DZ calculations, the calculated bond lengths are slightly longer than the measured ones, but there are good agreements between the calculated and measured bond angles. Thus, it seems that for complexes containing both the ylides and halides coordinated to Hg^{II}, the results of calculations with the LanL2DZ basis set is, as expected, more reliable than those derived from the LanL2MB calculations. The electronic energies of the mononuclear and corresponding binuclear complexes are given in *Table 10*. The results show that the products of the proposed reaction (*Eqn. 1*) are more stable than the reactants. These stabilities are *ca.* 30.5, 34.9, and 41.0 kcal/mol for X = Cl, Br, and I, respectively. Therefore, it is clear that for all compounds synthesized here, the gas-phase reaction shown in *Eqn. 1* is an exothermic reaction. Thus, it seems that the bridge-splitting reaction in DMSO solution is potentially possible for all dimeric complexes of bbtppy. The data also show that in the case of the I complex, the formation of the mononuclear complex is relatively more favorable than in the case of the corresponding Cl and Br complexes (*Table 10*).

Table 8. *Comparison of the Calculated Bond Lengths* ([Å]) *and Bond Angles* ([°]) *of* **3d** *with the Corresponding Experimental Values*[a])

	X-Ray	LanL2MB	LanL2DZ
Bond length [Å]:			
Hg(1)–I(1)	2.677	3.028	2.843
Hg(1)–I(2)	2.713	3.069	2.852
Hg(1)–O(2)	2.681	2.309	2.458
Hg(1)–C(1)	2.260	2.260	2.423
P(1)–C(23)	1.791	1.917	1.844
P(1)–C(1)	1.799	1.965	1.843
P(1)–C(9)	1.806	1.932	1.806
P(1)–C(16))	1.797	1.924	1.849
Bond angle [°]:			
I(1)–Hg(1)–I(2)	117.382	111.583	116.878
I(1)–Hg(1)–C(1)	119.316	114.141	118.314
I(1)–Hg(1)–C(2)	121.384	118.966	121.009
I(1)–Hg(1)–O(2)	97.948	102.442	99.309
O(1)–C(2)–C(1)	121.780	122.709	120.385
O(1)–C(2)–C(3)	120.606	120.740	118.817
C(23)–P(1)–C(1)	113.744	110.492	113.520
C(9)–P(1)–C(23)	108.004	109.634	108.920
C(23)–P(1)–C(16)	109.527	109.935	109.154
C(1)–P(1)–C(9)	111.405	111.289	111.696
C(16)–P(1)–C(1)	107.340	110.188	107.882
C(16)–P(1)–C(9)	106.578	105.175	105.315

[a]) See *Fig. 1* for the atom numbering.

Table 9. *Selected Calculated Bond Lengths* ([Å]) *and Bond Angles* ([°]) *of [HgX$_2$(bbtppy) (DMSO)]* (X = Cl, Br)[a])

	X = Cl		X = Br	
	LanL2MB	LanL2DZ	LanL2MB	LanL2DZ
Bond length [Å]:				
Hg(16)–X(19)	2.660	2.566	2.828	2.697
Hg(16)–X(24)	2.702	2.572	2.863	2.695
Hg(16)–O(62)	2.306	2.394	2.309	2.695
Hg(16)–C(11)	2.271	2.380	2.277	2.401
P(8)–C(9)	1.916	1.843	1.917	1.843
P(8)–C(10)	1.930	1.849	1.931	1.850
P(8)–C(11)	1.967	1.849	1.966	1.846
P(8)–C(7)	1.927	1.851	1.924	1.850
Bond angle [°]:				
X(19)–Hg(16)–X(24)	110.658	113.590	114.142	115.606
C(11)–Hg(16)–X(24)	107.507	119.583	110.617	118.901
C(11)–Hg(16)–Xl(19)	122.103	121.062	118.262	120.799
X(19)–Hg(16)–O(62)	98.093	97.534	100.137	98.231
O(23)–C(17)–C(25)	120.792	119.042	120.736	118.940
O(23)–C(17)–C(11)	122.557	120.393	122.747	120.379
C(7)–P(8)–C(9)	109.716	108.489	109.691	108.911
C(7)–P(8)–C(10)	107.649	106.523	105.515	105.793
C(7)–P(8)–C(11)	108.114	107.840	110.151	107.966
C(9)–P(8)–C(10)	109.279	109.146	109.707	109.118
C(9)–P(8)–C(11)	110.435	113.281	110.110	113.150
C(10)–P(8)–C(11)	111.587	111.294	111.565	111.602

[a]) See *Fig. 1* for the atom numbering.

Table 10. *Calculated Electronic Energies for Binuclear Complexes, DMSO, and Mononuclear Complexes*

X	[{HgX$_2$(bbtppy)}$_2$]	DMSO	[HgX$_2$(bbtppy)(DMSO)]	Δ*E* [kcal mol^{-1}][a])
Cl	– 2527.4032043	– 161.8305649	– 1425.5564682	30.50
Br	– 2520.317148	– 161.8305649	– 1422.0169333	34.88
I	– 2513.2343402	– 161.8305649	– 1418.4804131	41.01

[a]) Released energy in the gas-phase reaction of *Eqn. 1.*

$$[\{\mathrm{HgX_2(bbtppy)}\}_2] + 2\ \mathrm{DMSO} \xrightarrow{\text{gas phase}} 2\ [\mathrm{HgX_2(bbtppy)(DMSO)}] \qquad (1)$$

The calculated energies for HOMO and LUMO of [HgX$_2$(bbtppy)(DMSO)] (X = Cl and Br) are given in *Table 11*. The hardness η of a molecule is defined by *Eqn. 2*, where I and A are the ionization potential and the electron affinity of the system, respectively. Obviously, the energy gap between the HOMO and LUMO is equal to $(I - A)$. Thus, we can easily calculate the hardness of the present molecules by *Eqn. 3* [29].

Table 11. *Calculated Energies of HOMO and LUMO Molecular Orbitals, Hardness, and Energy Gap between the HOMO and LUMO of [HgX$_2$(bbtppy)(DMSO)] Complexes*

X	HOMO [hartree]	LUMO [hartree]	η [eV]	Gap [eV]
Cl	– 0.33545	0.06302	5.42	10.84
Br	– 0.32141	0.06256	5.22	10.44
I	– 0.29403	0.06122	4.83	9.66

$$\eta = \frac{(I - A)}{2} \tag{2}$$

$$\eta = \frac{(E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}})}{2} \tag{3}$$

We note that hard molecules have a large HOMO–LUMO gap, and soft molecules have a small one [30]. The results of the LanL2DZ calculation demonstrate that the HOMO and LUMO show up with a negative and positive charge, respectively (see *Table 11*). Furthermore, the calculated energy gap between these orbitals for complexes containing I is smaller than that for the other complexes. Thus, complexes including I as a ligand are softer than the other complexes described here. This is completely consistent with the fact that a hard group makes a molecule hard, and a soft group makes it soft. The HOMO and LUMO for all three mononuclear [HgX$_2$(bbtppy)(DMSO)] (X = Cl, Br, and I) complexes are illustrated in *Fig. 3*. It is interesting that the contribution of the coordinated halide in the HOMO increases from Cl to I, whereas the LUMO does not significantly change in the series of these complexes.

Conclusions. – The present study describes the synthesis and characterization of mononuclear and binuclear Hg$^{\mathrm{II}}$ complexes of phosphonium ylides. On the basis of the physicochemical and spectroscopic data, we propose that the herein described phosphonium ylide ligands exhibit monodentate *C*-coordination to the metal center. This study also presents a method for the synthesis of mononuclear Hg$^{\mathrm{II}}$ complexes of phosphonium ylides *via* a bridge-splitting reaction involving DMSO as ligand. Theoretical studies on the gas-phase structure of the complexes confirm that the bridge-splitting reaction in DMSO solution is potentially possible for all dimeric complexes in which DMSO can act as a ligand.

Experimental Part

General. All reactions were performed in air. Starting materials were purchased from commercial sources and used without further purification. All solvents were dried by reported methods [31]. M.p.: *SMPI* apparatus; uncorrected. FT-IR Spectra: *Shimadzu-435* spectrophotometer; KBr pellets; $\tilde{\nu}$ in cm^{-1}. ^{1}H-, ^{13}C- and ^{31}P-NMR Spectra: *Bruker-200* and *Jeol-90* spectrometer; δ in ppm rel. to Me$_4$Si as internal standard, *J* in Hz. Elemental analysis: *Perkin-Elmer 2400* analyzer for C, H, and N.

*[(2-Thienylcarbonyl)methylene]tri(*p*-tolyl)phosphorane* (*=1-(2-Thienyl)-2-[tris(4-methylphenyl)-phosphoranylidene]ethanone*; tptpy). To a soln. of 2-(bromoacetyl)thiophene (0.102 g, 0.5 mmol) in

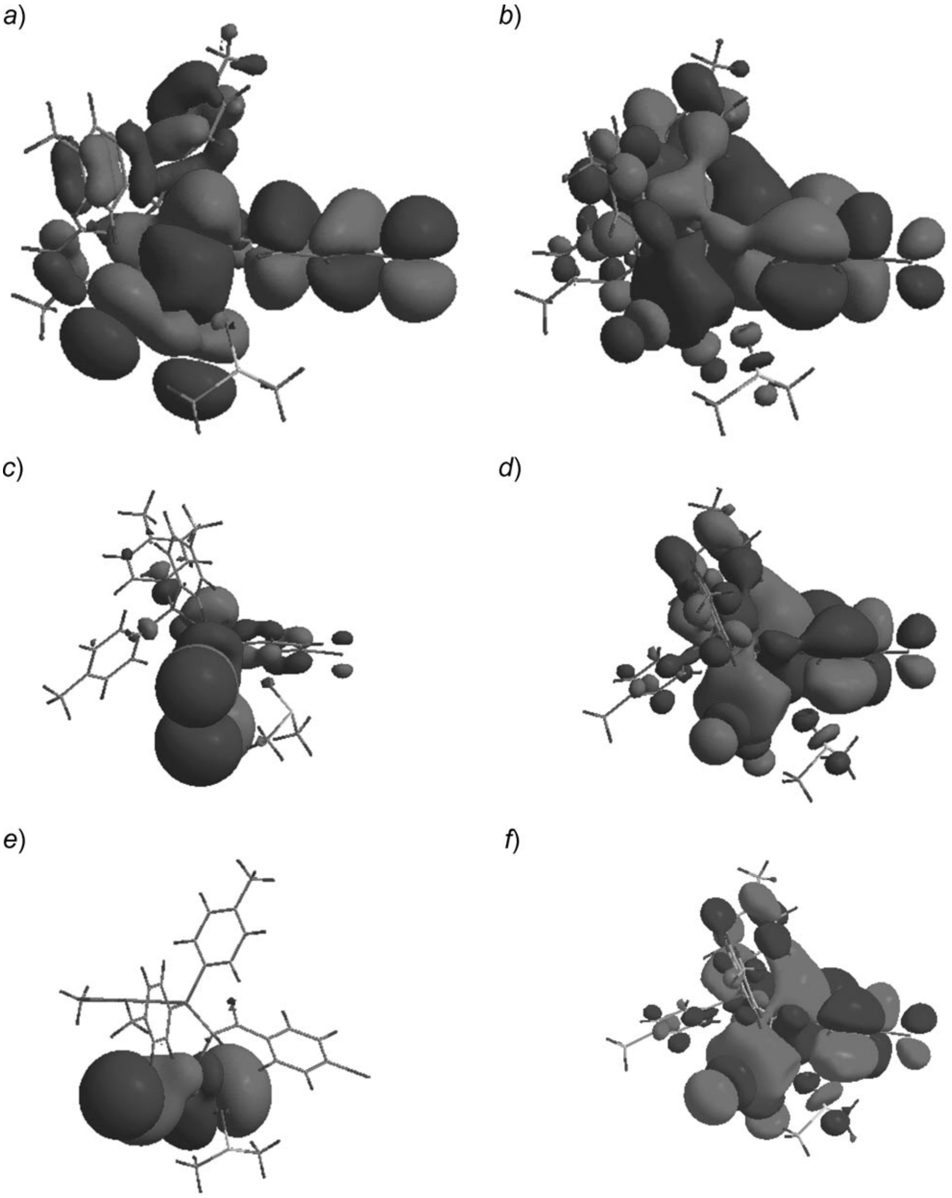


Fig. 3. a) c) e) *Calculated HOMOs and* b) d) f) *LUMOs for compounds [HgX$_2$(bbtppy)(DMSO)], where X = Cl (a, b), Br (c, d), and I (e, f), respectively*

acetone (10 ml) was added a soln. of tri(*p*-tolyl)phosphine (0.152 g, 0.5 mmol) in the same solvent (5 ml). The brown soln. was stirred at r.t. for 12 h. The suspension was concentrated to 3 ml. After addition of Et$_2$O, the precipitate was filtered off, washed with Et$_2$O (2 × 10 ml), and dried under reduced pressure.

Further treatment with aq. NaOH soln. (0.5M) led to elimination of HBr, giving the free ligand tptpy (83%). M.p. 179–180°. Anal. calc. for $C_{27}H_{25}OPS$ (428.53): C 75.68, H 5.88; found: C 75.70, H 5.84.

[(Furan-2-ylcarbonyl)methylene]triphenylphosphorane (=*1-[(Furan-2-yl)-2-(triphenylphosphoranylidene]ethanone*; fppy). As described for TPTPY, with 2-bromo-1-(furan-2-yl)ethanone (0.094 g, 0.5 mmol), acetone (10 ml), triphenylphosphine (0.131 g, 0.5 mmol), and acetone (5 ml), at r.t. for 4 h: fppy (74%). M.p. 219–221°. Anal. calc. for $C_{24}H_{19}O_2P$ (370.38): C 77.83, H 5.17; found: C 76.31, H 4.98.

*[(4-Bromobenzoyl)methylene]tri(*p*-tolyl)phosphorane* (=*1-(4-Bromophenyl)-2-[tris(4-methylphenyl)phosphoranylidene]ethanone*; bbtppy). To a soln. of tri(*p*-tolyl)phosphine (0.152 g, 0.5 mmol) in $CHCl_3$ (25 ml) was added 1-(4-bromophenyl)ethanone (0.139 g, 0.5 mmol), and the resulting mixture was stirred for 12 h. The soln. was filtered off, and the precipitate was washed with Et_2O and dried. Further treatment with aq. NaOH soln. (0.5M) led to elimination of HBr, giving the free ligand bbtppy (85%). M.p. 177–179°. Anal. calc. for $C_{29}H_{26}BrOP$ (501.39): C 69.47, H 5.23; found: C 69.46, H 5.13.

Complexes **1**–**3**: *General Procedure.* The binuclear complexes were prepared by the following general procedure and their structures suggested according to [14][15][32]. To tptpy (0.107 g, 0.25 mmol) in MeOH (5 ml) was added $HgCl_2$ (0.067 g, 0.25 mmol). The mixture was stirred at r.t. for 4 h. The formed dimeric complex **1a** was separated by filtration and washed with Et_2O. The corresponding bromo and iodo complexes were prepared with $HgBr_2$ (0.09 g, 0.25 mmol) and HgI_2 (0.11 g, 0.25 mmol), resp., in the same manner.

Di-μ-chlorodichlorobis{2-oxo-2-(2-thienyl)-1-[tris(4-methylphenyl)phosphonio]ethyl}dimercury ([{$HgCl_2$ (tptpy)}$_2$]; **1a**): Yield 72.4%. M.p. 179–180°. Anal. calc. for $C_{54}H_{50}Cl_4Hg_2O_2P_2S_2$ (1400.04): C 46.33, H 3.60; found: C 45.33, H 3.75.

Di-μ-bromodibromobis{2-oxo-2-(2-thienyl)-1-[tris(4-methylphenyl)phosphonio]ethyl}dimercury ([{$HgBr_2$ (tptpy)}$_2$]; **1b**): Yield 66.2%. M.p. 200–201°. Anal. calc. for $C_{54}H_{50}Br_4Hg_2O_2P_2S_2$ (1577.85): C 41.11, H 3.19; found: C 42.32, H 3.05.

Di-μ-iododiiodobis{2-oxo-2-(2-thienyl)-1-[tris(4-methylphenyl)phosphonio]ethyl}dimercury ([{HgI_2 (tptpy)}$_2$]; **1c**): Yield 57%. M.p. 193–195°. Anal. calc. for $C_{54}H_{50}Hg_2I_4O_2P_2S_2$ (1765.85): C 36.73, H 2.85; found: C 36.69, H 2.83.

Di-μ-chlorodichlorobis{2-(furan-2-yl)-2-oxo-1-(triphenylphosphonio)ethyl}dimercury ([{$HgCl_2$ (fppy)}$_2$]; **2a**): Yield 64%. M.p. 218–219°. Anal. calc. for $C_{48}H_{38}Cl_4Hg_2O_4P_2$ (1283.75): C 44.91, H 2.98; found: C 45.41, H 2.82.

Di-μ-bromodibromobis{2-(furan-2-yl)-2-oxo-1-(triphenylphosphonio)ethyl}dimercury ([{$HgBr_2$ (fppy)}$_2$]; **2b**): Yield 56.1%. M.p. 213–215°. Anal. calc. for $C_{48}H_{38}Br_4Hg_2O_4P_2$ (1461.56): C 39.45, H 2.62; found: C 39.72, H 2.54.

Di-μ-iododiiodobis{2-(furan-2-yl)-2-oxo-1-(triphenylphosphonio)ethyl}dimercury ([{HgI_2 (fppy)}$_2$]; **2c**): Yield 48.1%. M.p. 198–199°. Anal. calc. for $C_{48}H_{38}Hg_2I_4O_4P_2$ (1649.56): C 34.95, H 2.32; found: C 35.3, H 2.23.

Di-μ-chlorodichlorobis{2-(4-bromophenyl)-2-oxo-1-[tris(4-methylphenyl)phosphonio]ethyl}dimercury ([{$HgCl_2$ (bbtppy)}$_2$]; **3a**): Yield 67%. M.p. 182–184°. Anal. calc. for $C_{58}H_{52}Br_2Cl_4Hg_2P_2O_2$ (1545.78): C 45.07, H 3.39; found: C 45.06, H 3.38.

Di-μ-bromodibromobis{2-(4-bromophenyl)-2-oxo-1-[tris(4-methylphenyl)phosphonio]ethyl}dimercury ([{$HgBr_2$ (bbtppy)}$_2$]; **3b**): Yield 64%. M.p. 189–191°. Anal. calc. for $C_{58}H_{52}Br_6Hg_2P_2O_2$ (1723.58): C 40.42, H 3.04; found: C 40.82, H 3.00.

Di-μ-iododiiodobis{2-(4-bromophenyl)-2-oxo-1-[tris(4-methylphenyl)phosphonio]ethyl}dimercury ([{HgI_2 (bbtppy)}$_2$]; **3c**): Yield 64%. M.p. 184–186 . Anal. calc. for $C_{58}H_{52}Br_2Hg_2I_4P_2O_2$ (1911.59): C 36.44, H 2.74; found: C 36.51, H 2.77.

{2-(4-Bromophenyl)-2-oxo-1-[tris(4-methylphenyl)phosphonio]ethyl}{(sulfinyl-κO)bis[methane]}-mercury ([HgI_2 (bbtppy) (DMSO)]; **3d**). The binuclear complex **3c** (0.191 g, 0.1 mmol) was dissolved in DMSO (2 ml). Colorless crystals were formed by slow evaporation of the solvent over several days: 0.198 g (96%) of **3d**. M.p. 180° (dec.). Anal. calc. for $C_{31}H_{32}BrHgI_2O_2PS$ (1033.93): C 36.01, H 3.12; found: C 35.92, H 3.25.

X-Ray Crystal-Structure Determination of **3d**¹). The single-crystal X-ray diffraction analysis of a suitable crystal of **3d** was performed with a *Stoe-IPDS-II* two-circle diffractometer at 298 K and graphite monochromated MoK_α radiation (λ 0.7107 Å). The data collection was performed at r.t. with the ω-scan technique and the X-AREA software package [28]. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 by SHELX [33] and with the X-STEP32 crystallographic software package [34]. All non-H-atoms were refined anisotropically with reflections $I > 2\sigma(I)$. H-Atoms were inserted at calculated positions in a riding mode with fixed thermal parameters.

Theoretical Studies. The geometries of the compounds were fully optimized at the *Hartree–Fock* (*HF*) level of theory with the GAUSSIAN98 program [35] on a *Pentium* personal computer with a 3600 MHz processor. The standard LanL2DZ basis set was used for all complexes [17]. This basis set includes effective core potentials (ECP) for both the mercury and phosphorus as well as halide (Cl, Br and I) ions. Vibrational-frequency analyses, calculated at the same level of theory, indicate that optimized structures are at the stationary points corresponding to local minima, without any imaginary frequency. Atomic coordinates for *ab initio* calculations were obtained from the data of the X-ray crystal-structure analyses.

REFERENCES

[1] E. P. Urriolabeitia, *J. Chem. Soc., Dalton Trans.* **2008**, 5673.

[2] O. I. Kolodiazhnyi, *Tetrahedron* **1996**, *52*, 1855.

[3] A. W. Johnson, 'Ylides and Imines of Phosphorus', Wiley, New York, 1993, Chapt. 14 and refs. cit. therein.

[4] H.-J. Cristau, *Chem. Rev.* **1994**, *94*, 1299.

[5] 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.

[6] S. Kato, T. Kato, M. Mizuta, K. Itoh, Y. Ishii, *J. Organomet. Chem.* **1973**, *51*, 167.

[7] J. A. Albanese, A. L. Rheingold, J. L. Burmeister, *Inorg. Chim. Acta* **1988**, *150*, 213.

[8] M. Kalyanasundari, K. Panchanatheswaran, W. T. Robinson, H. Wen, *J. Organomet. Chem.* **1995**, *491*, 103.

[9] R. Usón, J. Forniés, R. Navarro, P. Espinet, C. Mendívil, *J. Organomet. Chem.* **1985**, *290*, 125.

[10] H. Koezuka, G. Matsubayashi, T. Tanaka, *Inorg. Chem.* **1976**, *25*, 417.

[11] J. Vicente, M. T. Chicote, J. Fernandez-Baeza, J. Martin, I. Saura-LIamas, J. Turpin, P. G. Jones, *J. Organomet. Chem.* **1987**, *331*, 409.

[12] J. Vicente, M. T. Chicote, I. Saura-LIamas, J. Turpin, J. Fernandez-Baeza, *J. Organomet. Chem.* **1987**, *333*, 129.

[13] J. A. Albanese, D. L. Staley, A. L. Rheingold, J. L. Burmeister, *Inorg. Chem.* **1990**, *29*, 2209.

[14] S. J. Sabounchei, A. Dadrass, M. Jafarzadeh, S. Salehzadeh, H. R. Khavasi, *J. Organomet Chem.* **2007**, *692*, 2500.

[15] S. J. Sabounchei, V. Jodaian, H. R. Khavasi, *Polyhedron* **2007**, *26*, 2845.

[16] L. Fälth, *Chem. Scr.* **1976**, *9*, 71.

[17] J. B. Collins, P. von R. Schleyer, J. S. Binkley, J. A. Pople, *J. Chem. Phys.* **1976**, *64*, 5142.

[18] T. S. Lobana, M. K. Sandhu, M. J. Liddell, E. R. T. Tiekink, *J. Chem. Soc., Dalton Trans.* **1990**, 691.

[19] S. J. Sabounchei, H. Nemattalab, S. Salehzadeh, M. Bayat, H. R. Khavasi, H. Adams, *J. Organomet. Chem.* **2008**, *693*, 1975.

[20] P. Laavanya, U. Venkatasubramanian, K. Panchanatheswaran, J. A. K. Bauer, *Chem. Commun.* **2001**, 1660.

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

---

¹) CCDC-664083 contains the supplementary crystallographic data for complex **3d**. These data can be obtained free of charge from the *Cambridge Crystallographic Data Center via* http://www.ccdc.cam.ac.uk/data_request/cif.

[22] M. Calligaris, O. Carugo, *Coord. Chem. Rev.* **1996**, *153*, 83.

[23] E. Alessio, G. Mestroni, G. Nardin, W. M. Attia, M. Calligaris, G. Sava, S. Zorzet, *Inorg. Chem.* **1988**, *27*, 4099.

[24] E. Alessio, B. Milani, M. Bolle, G. Mestroni, P. Faleschini, F. Todone, S. Geremia, Calligaris, *Inorg. Chem.* **1995**, *34*, 4722.

[25] B. Serli, E. Zangrando, E. Iengo, G. Mestroni, L. Yellowlees, E. Alessio, *Inorg. Chem.* **2002**, *41*, 4033.

[26] B. Serli, E. Zangrando, E. Iengo, E. Alessio, *Inorg. Chim. Acta* **2002**, *339*, 265.

[27] M. Calligaris, N. S. Panina, *J. Mol. Struct.* **2003**, *646*, 61.

[28] X-AREA, Version 1.30, Program for the Acquisition and Analysis of Data, Stoe & Cie GmbH, Darmstadt, Germany, 2005.

[29] R. G. Pearson, *Inorg. Chem.* **1988**, *27*, 734.

[30] P. K. Chattaraj, A. Poddar, *J. Phys. Chem. A* **1999**, *103*, 8691

[31] A. J. Gordon, R. A. Ford, 'The Chemist's Companion – A Handbook of Practical Data, Techniques and References', Wiley – Interscience, New York, 1972, p. 438.

[32] E. C. Spencer, M. B. Mariyatra, J. A. K. Howard, A. M. Kenwright, K. Panchanatheswaran, *J. Organomet. Chem.* **2007**, *692*, 1081.

[33] G. M. Sheldrick, SHELX97, Program for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1997.

[34] X-STEP32, Version 1.07b, Crystallographic Package, Stoe & Cie GmbH, Darmstadt, Germany, 2005.

[35] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratman, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Menucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Ciolowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzales, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Repogle, J. A. Pople, GAUSSIAN 98, Revision A.6, Gaussian Inc., Pittsburgh, PA, 1998.

[36] M. Calligaris, A. Melchior, S. Geremia, *Inorg. Chim. Acta* **2001**, *323*, 89.

Received August 26, 2009