

*In The Name of Allah,
The Most Beneficent, The
Most merciful*

H.A.K



Bu-Ali Sina University
Faculty of Chemistry

**Thesis for the Degree of Doctor of Philosophy in
Inorganic Chemistry**

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**Synthesis and characterization of some new
phosphorus ylides and their metal
complexes with spectroscopy and X-ray
crystallography methods**

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Bu-Ali Sina University
Faculty of Chemistry

Synthesis and characterization of a number of new
phosphorus ylides and their metal complexes by
spectroscopy and X-ray crystallography methods

Thesis submitted in partial fulfillment of the requirements for the degree of doctor of
philosophy (Ph.D.) in Inorganic Chemistry

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To my Wife,

Samira

And my Daughter,

Hasti

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Abstract

After presentation of a history of phosphorus ylides and their metal complexes, the synthesis of 12 keto-stabilized phosphorus ylides with general formula of Ar_3PCHCOR (α type) and $\text{Ar}_3\text{PCO}_2\text{R}^1\text{CHR}^2\text{CO}_2\text{R}^1$ (β -type) (Ar = aryl group; R=aryl or alkyl groups; R^1 and R^2 =alkyl groups) are presented. Characterization of above ylides were performed with elemental analysis, IR, ^1H NMR, ^{31}P NMR and ^{13}C NMR spectroscopy methods. Variable temperature ^1H and ^{31}P NMR study on one of the β -type, shows that the two rotamers equilibrate rapidly at higher temperatures. The crystal structure of one of the α types is also discussed.

The synthesis of thirteen binuclear, three mononuclear and four polynuclear complexes of α -ylides are reported. Characterization of these compounds were performed with elemental analysis, IR, ^1H NMR, ^{31}P NMR and ^{13}C NMR spectroscopy methods. The existence of satellites due to coupling between ^{199}Hg and ^{31}P centers at room temperature and disappearing of them in ^{31}P NMR spectra at higher temperatures and lower concentrations is a new observation in Hg(II) complexes of phosphorus ylides.

The crystal structure of three binuclear, three mononuclear and one polynuclear Hg(II) complexes of these ylides are discussed. Furthermore, the crystal structure of two previously known binuclear complexes and one orthopalladated complex are also studied. These studies show that:

- 1- C-coordination is occurred for all ligands coordinated to Hg(II), Cd(II) and Pd(II) centers.
- 2- An unprecedented O-coordination of DMSO to a soft Hg(II) center is occurred.
- 3- Presentation of a coordination number of 7 for Hg(II) in polymeric complex with bridged nitrate anions is interesting and unusual.
- 4- Comparing of bond lengths in free ylide and coordinated ylide in Hg(II) complex indicates that ylide resonance forms are destroyed upon complexation.

Ab initio calculations were made on the mercury(II) complexes of phosphorus ylides. Following results were obtained:

- 1- Calculations on binuclear Hg(II) complexes show that the observed trans-like isomers are always more stable than cis-like ones. This stability is calculated to be 4-12 Kcal.mol⁻¹.
- 2- The results of calculation show that the bridge-splitting exothermic reaction in DMSO solution is potentially possible for all dimeric complexes in which DMSO acts as a ligand. The data show that in the case of iodine complexes, the formation of mononuclear complexes is relatively more favorable than corresponding chlorine and bromine complexes.
- 3- We were interested to compare the relative stability of two possible C- and O-coordinated isomers in binuclear Hg(II) complexes of phosphorus ylides. Thus we optimized an O-coordinated structural isomer for one of compounds. The results showed that this structure is 49.63 Kcal/mol less stable than its observed C-coordinated isomer indicating that C-coordination is significantly preferred with all ligands in present complexes.

Table of contents

	page
<i>List of Tables</i>	V
<i>List of Figures</i>	VII
<i>List of Appendixes</i>	IX
<i>Abbreviations</i>	XIV
Chapter One: Phosphorus Ylides and their Metal Complexes	
1.1. Introduction	2
1.2. Phosphorus ylides	4
1.2.1 Carbonyl stabilized phosphorus ylide	5
1.2.2. Phosponium bis ylides	6
1.2.3. β -phosphorus ylides	7
1.2.4. Doubly keto-stabilized phosphorus ylides	8
1.3. Phosponium ylides in coordination chemistry	9
1.3.1. Metal-C(yilde) coordination	10
1.3.1.1. Pd(II) and Pt(II) complexes of carbonyl-stabilized phosphorus ylides	10
1.3.1.2. Gold(I) complexes of keto-stabilized phosphorus ylide	15
1.3.1.3 Iron complexes of phosphorus ylides	16
1.3.1.4. Mercury (II) complexes of phosphorus ylides	17
1.3.2. Metal-O(ylide) coordination	20
1.3.2.1. Ylides and group 4 transition metals	21
1.3.2.2. Synthesis and characterization of {[Pd (dmba)(py)(O-APPY)]} (ClO ₄), unusual O-coordination of the acethyl methylenetriphenylephosphorane ligand to a soft metal center	22
1.3.2.3. The unprecedented O-coordinated of α -acetyl- α -benzoylmethylenetri phenylphosphorane (ABPPY) to Hg(II)	23
1.3.3 Chelating systems	25
1.3.4. Orthometallation	27
1.4. Metal-C (ylide) versus metal-O(ylide) coordination	29
References	30

Chapter Two: Synthesis and Characterization of α- and β-Keto-Stabilized Phosphorus Ylides by Spectroscopy and X-ray Diffraction Methods	38
2.1. Introduction	39
2.2. Experimental	40
2.2.1. Materials	40
2.2.2. Physical measurements	40
2.2.3. Synthesis of α -keto-stabilized ylides (general procedure)	41
2.2.3.1. Synthesis and characterization of $[\text{ClC}_6\text{H}_4\text{COCH}_2\text{PPh}_3]\text{Br}$ (1)	42
2.2.3.2. Synthesis and characterization of $\text{ClC}_6\text{H}_4\text{COCHPPh}_3$ (2)	42
2.2.3.3. Synthesis and characterization of $[\text{ClC}_6\text{H}_4\text{COCH}_2\text{P}(p\text{-tolyl})_3]\text{Br}$ (3)	43
2.2.3.4. Synthesis and characterization of $\text{ClC}_6\text{H}_4\text{COCHP}(p\text{-tolyl})_3$ (4)	44
2.2.3.5. Synthesis and characterization of $[\text{NO}_2\text{C}_6\text{H}_4\text{COCH}_2\text{PPh}_3]\text{Br}$ (5)	44
2.2.3.6. Synthesis and characterization of $\text{NO}_2\text{C}_6\text{H}_4\text{COCHPPh}_3$ (6)	45
2.2.3.7. Synthesis and characterization of $[\text{NO}_2\text{C}_6\text{H}_4\text{COCH}_2\text{P}(p\text{-tolyl})_3]\text{Br}$ (7)	46
2.2.3.8. Synthesis and characterization of $\text{NO}_2\text{C}_6\text{H}_4\text{COCHP}(p\text{-tolyl})_3$ (8)	47
2.2.4. Synthesis of β -keto-stabilized phosphorus ylides	47
2.2.4.1. Dimethyl 2-(phtalimid- <i>N</i> -yl)-3-(triphenylphosphanylidene)-butane dioate (6a) (typical procedure)	48
2.2.4.2. Dimethyl 2-(<i>N,N'</i> -diacetylhydrazine- <i>N</i> -yl)-3-(triphenyl phosphanyli dene)-butanedioate (6b)	49
2.2.4.3. Dimethyl 2-(phtalimid- <i>N</i> -yl)-3-(tri- <i>p</i> -tolylphosphanylidene)-butane dioate (6c)	49
2.2.4.4. Dimethyl 2-(<i>N,N'</i> -diacetylhydrazine- <i>N</i> -yl)-3-(tri- <i>p</i> -tolyl phosphan-ylidene)-butanedioate (6d)	50
2.2.4.5. Di-tert-butyl 2-(phtalimid- <i>N</i> -yl)-3-(triphenylphosphanylidene)-butanedioate (6e)	51
2.2.4.6. Di-tert-butyl 2-(<i>N,N'</i> -diacetylhydrazine- <i>N</i> -yl)-3-(triphenyl phosphanylidene)-butanedioate (6f)	51
2.2.4.7. Di-tert-butyl 2-(phtalimid- <i>N</i> -yl)-3-(tri- <i>p</i> -tolylphosphanylidene)-butanedioate (6g)	52
2.2.4.8. Di-tert-butyl 2-(<i>N,N'</i> -diacetylhydrazine- <i>N</i> -yl)-3-(tri- <i>p</i> -tolyl phosphanylidene)-butanedioate (6h)	52
2.3. Results and discussion	53

2.3.1. α -keto-stabilized phosphorus ylides	53
2.3. β -keto-stabilized phosphorus ylides	57
References	59
Chapter Three: Synthesis and Characterization of Some Metal Complexes of Phosphorus Ylides	63
3.1. Introduction	64
3.1.1. Binuclear complexes	65
3.1.2. Mononuclear complexes	69
3.1.3. Trinuclear complexes	70
3.1.4. Complexes derived from the phosphonium salts	70
3.2. Experimental	72
3.2.1. Materials	72
3.2.2. Physical measurements	73
3.2.3. Synthesis and characterization of binuclear Hg(II) complexes of phosphorus ylides	73
3.2.3.1. Synthesis and characterization of $[(Y_1).HgCl_2]_2$ (1), general procedure	74
3.2.3.2. Synthesis and characterization of $[(Y_1).HgBr_2]_2$ (2)	75
3.2.3.3. Synthesis and characterization of $[(Y_1).HgI_2]_2$ (3)	76
3.2.3.4. Synthesis and characterization of $[(Y_2).HgCl_2]_2$ (4)	76
3.2.3.5. Synthesis and characterization of $[(Y_2).HgBr_2]_2$ (5)	77
3.2.3.6. Synthesis and characterization of $[(Y_2).HgI_2]_2$ (6)	78
3.2.3.7. Synthesis and characterization of $[(Y_3).HgCl_2]_2$ (7)	81
3.2.3.8. Synthesis and characterization of $[(Y_3).HgBr_2]_2$ (8)	82
3.2.3.9. Synthesis and characterization of $[(Y_3).HgI_2]_2$ (9)	83
3.2.3.10. Synthesis and characterization of $[(Y^4).HgCl_2]_2$ (10)	86
3.2.3.11. Synthesis and characterization of $[(Y^4).HgBr_2]_2$ (11)	87
3.2.3.12. Synthesis and characterization of $[(Y^4).HgI_2]_2$ (12)	91
3.2.3.13. X-ray crystal structure of $[(Y^5).HgBr_2]_2$ (13)	91
3.2.3.14. X-ray crystal structure of $[(Y^5).HgI_2]_2$ (14)	94
3.2.4. Synthesis and characterization of mononuclear Hg(II) complexes of phosphorus ylides	97
3.2.4.1. Synthesis and characterization of $[(Y^1).HgCl_2.DMSO]$ (15)	98

3.2.4.2. Synthesis and characterization of $[(Y^1).HgI_2.DMSO]$ (16)	101
3.2.4.3. Synthesis and characterization of $[(Y^2).HgI_2.DMSO]$ (17)	105
3.2.5. Synthesis and characterization of polynuclear Hg(II) complexes of phosphorus ylides	108
3.2.5.1. Synthesis and characterization of $[(Y^1).Hg(NO_3)_2]_n$ (18)	109
3.2.5.2. Synthesis and characterization of $[(Y^2).Hg(NO_3)_2]_n$ (19)	112
3.2.5.3. Synthesis and characterization of $[(Y^3).Hg(NO_3)_2]_n$ (20)	113
3.2.5.4. Synthesis and characterization of $[(Y^4).Hg(NO_3)_2]_n$ (21)	114
3.2.6. Synthesis and characterization of Cd(II) and Pd(II) complexes of phosphorus ylides	114
3.2.6.1. Synthesis and characterization of $[(Y^1).CdCl_2]_2$ (22)	114
3.2.6.2. X-ray crystal structure of $[Pd\{CH\{P(C_7H_6)(p\text{-tolyl})_2\}COCH_3\}ClP(p\text{-tolyl})_3]$ (23)	115
3.3. Results and discussion	118
3.3.1. Spectroscopy	118
3.3.2. X-ray crystallography	124
References	128
Chapter Four: Theoretical Study on Mercury(II) Complexes of α-Keto-Stabilized Phosphorus Ylides	134
4.1. Introduction	135
4.2. Basis set	137
4.2.1. Minimal basis sets	138
4.2.2. Split valance basis sets	138
4.2.3. Polarized basis sets	139
4.2.4. Basis sets for post-third-row atoms	139
4.3. Theoretical studies on some of mercury(II) complexes of phosphorus ylides	139
4.3.1. Energy difference between the trans- and cis-like structures in binuclear complexes	140
4.3.2. Comparison of the energy deference between the mononuclear compounds containing DMSO as ligand and parent binuclear complexes	149
4.3.3. Comparison of the relative stability of two possible C- and O-coordinated isomers.	154
References	157

List of Tables

Table 1.1. The important phosphorus ylides	6
Table 2.1. Ylide components 6a-h	48
Table 2.2. ν CO and ν P-C of selected phosphonium salts and phosphoranes (cm^{-1})	53
Table 2.3. Crystallographic data summary for compound 2	55
Table 2.4. Selected bond distances (\AA) and angles ($^\circ$) for $\text{ClC}_6\text{H}_4\text{COCHPPh}_3$	57
Table 3.1. Crystallographic data summary for 6	80
Table 3.2. Selected bond lengths (\AA) and angles ($^\circ$) for 6	81
Table 3.3. Crystallographic data summary for 9	85
Table 3.4. Selected bond lengths (\AA) and angles ($^\circ$) for 9	86
Table 3.5. Selected key bond lengths (\AA) and angles ($^\circ$) for $[(\text{Y}^4)\cdot\text{HgBr}_2]_2\cdot 2\text{DMSO}$ (11)	88
Table 3.6. Crystallographic data summary for 11	90
Table 3.7. Selected key bond lengths (\AA) and angles ($^\circ$) for $[(\text{Y}^4)\cdot\text{HgBr}_2]_2\cdot 2\text{DMSO}$ (11)	93
Table 3.8. Selected key bond lengths (\AA) and angles ($^\circ$) for $[(\text{Y}^5)\cdot\text{HgBr}_2]_2$ (13)	94
Table 3.9. Crystallographic data summary for 14	96
Table 3.10. Selected bond lengths (\AA) and angles ($^\circ$) for 14	97
Table 3.11. Crystallographic data summary for 15	100
Table 3.12. Selected bond lengths (\AA) and angles ($^\circ$) for 15	101
Table 3.13. Selected key bond lengths (\AA) and bond angles ($^\circ$) for 16	102
Table 3.14. Crystallographic data summary for 16	104
Table 3.15. Crystallographic data summary for 17	107
Table 3.16. Selected bond lengths (\AA) and angles ($^\circ$) for 17	108
Table 3.17. Crystallographic data summary for complex 18	111
Table 3.18. Selected bond lengths (\AA) and angles ($^\circ$) for 18	112
Table 3.19. Crystal data and structure refinement for 23	117
Table 3.20. Selected bond lengths (\AA) and angles ($^\circ$) for 23	118
Table 3.21. The $\nu(\text{CO})$ and $\nu(\text{P-C})$ for ylides and related complexes	119
Table 3.22. The ^1H NMR and ^{31}P NMR data of the complexes together with those of the parent ylides	120
Table 3.23. ^{31}P NMR data of the complexes together with those of the parent ylides	120
Table 3.24. ^{13}C NMR data of the complexes together with those of the parent ylides	123

Table 3.25. Comparison of bond lengths (Å) in different Hg(II) halide complexes of phosphorus ylides	124
Table 4.1. A comparison between the calculated bond lengths (Å) and bond angles (°) with corresponding experimental values for compound 3	145
Table 4.2. A comparison between the selected calculated bond lengths (Å) and bond angles (°) for the compound 5 with corresponding experimental values	145
Table 4.3. A comparison between the selected calculated bond lengths (Å) and bond angles (°) for the compound 8 with corresponding experimental values	146
Table 4.4. A comparison between the selected calculated bond lengths (Å) and bond angles (°) for the compound 9 with corresponding experimental values	146
Table 4.5. Selected key bond lengths and angles for trans-like molecular structure of 1 and 2	147
Table 4.6. Selected key bond lengths and angles for trans-like molecular structure of 4 and 6	147
Table 4.7. Selected key bond lengths and angles for trans-like molecular structures of 7	148
Table 4.8. A comparison between energies of trans- and cis-like isomers	149
Table 4.9. A comparison between the calculated bond lengths (Å) and bond angles (°) for compound 5 with corresponding experimental values	152
Table 4.10. A comparison between the calculated bond lengths (Å) and bond angles (°) for compound 15 with corresponding experimental values	152
Table 4.11. Selected calculated key bond lengths and angles for structures 11 and 12	153
Table 4.12. Calculated selected key bond lengths and angles for molecular structures of [(Y").HgX ₂ .DMSO] (X = Cl and Br)	153
Table 4.13. Calculated electronic energies for binuclear complexes, DMSO and mononuclear complexes involved in Eq. 4.1	154
Table 4.14. Comparison of important characteristic calculated bond lengths for observed C-coordinated and its unobserved O-coordinated isomer isomers	156

List of figures

Fig.1.1. Structure of complex [(EPPY)(HgX ₂) ₂]. Hydrogen atoms and the second solvent molecule are excluded for clarity	18
Fig. 1.2. ORTEP view of X-ray crystal structure of complex [((<i>p</i> -tolyl) ₃ PCHCOOCH ₂ C ₆ H ₅).HgBr ₂] ₂	19
Fig. 1.3. ORTEP view of X-ray crystal structure of complex [(Ph ₃ PCHCOC ₆ H ₄ OCH ₃).HgBr ₂] ₂ .2(C ₂ H ₅) ₂ O	19
Fig. 1.4. ORTEP view of X-ray crystal structure of complex [(Ph ₃ PCHCOC ₆ H ₄ OCH ₃).HgCl ₂] ₂	20
Fig.1.5. ZORTEP view of chloro complex [HgCl ₂ (ABPPY) ₂] with 50% probability thermal ellipsoids and selected atom labeling scheme	23
Fig. 1.6. ZORTEP view of bromo complex [HgBr ₂ (ABPPY) ₂] with 50% probability thermal ellipsoids and selected atom labelling scheme	24
Fig. 2.1. ORTEP view of the X-ray crystal structure of ClC ₆ H ₄ COCHPPH ₃	56
Fig. 2.2. Packing diagram of ClC ₆ H ₄ COCHPPH ₃	56
Fig. 2.3. Variable temperature NMR study on 6a in CDCl ₃ : a) ³¹ P NMR, b) ¹ H NMR (doublet of CH)	58
Fig. 3.1. ORTEP view of X-ray crystal structure of [BPPY.HgCl ₂] ₂ .2CH ₃ OH	66
Fig. 3.2. ORTEP view of X-ray crystal structure of [BPPY.HgI ₂] ₂	66
Fig. 3.3. ORTEP view of X-ray crystal structure of [(Ph ₃ PC(H)C(O)C ₆ H ₄ OCH ₃).HgBr ₂] ₂	67
Fig. 3.4. ORTEP view of X-ray crystal structure of [((<i>p</i> -tolyl) ₃ PC(H)C(O)OCH ₂ Ph).HgBr ₂] ₂	68
Fig. 3.5. ZORTEP view of chloro complex [HgCl ₂ (ABPPY) ₂] with 50% probability thermal ellipsoids and selected atom labeling scheme	70
Fig. 3.6. ORTEP view of X-ray crystal structure of [(BPPY) ₂ .(HgI ₂) ₃]	70
Fig. 3.7. ORTEP view of X-ray crystal structure of [((<i>p</i> -tolyl) ₃ PCH ₂ C(O)C ₆ H ₄ OCH ₃) ₂ .Hg ₂ I ₆]	71
Fig. 3.8. ORTEP view of X-ray crystal structure of [(Ph ₃ PCH ₂ C(O)C ₆ H ₄ Br) ₂ .Hg ₂ Br ₆]	71
Fig. 3.9. ORTEP view and packing diagram of [(Y ²).HgI ₂] ₂	79
Fig. 3.10. ORTEP view and packing diagram of [(Y ³).HgI ₂] ₂	84
Fig. 3.11. ORTEP view and packing diagram of [(Y ⁴).HgBr ₂] ₂ .2DMSO	89
Fig. 3.12. ORTEP view and packing diagram of [(Y ⁵).HgBr ₂] ₂ (13)	92

Fig. 3.13. ORTEP view and packing diagram of $[(Y^5).HgI_2]_2$ (14)	95
Fig. 3.14. ORTEP view and packing diagram of $[(Y^1).HgCl_2]_2$ (15)	99
Fig. 3.15. ORTEP view and packing diagram of $[(Y^1).HgI_2]_2$ (16)	103
Fig. 3.16. ORTEP view and packing diagram of $[(Y^2).HgI_2.DMSO]$ (17)	106
Fig. 3.17. X-Ray Crystal structure of 18. (a) Asymmetric unit, (b) Polymeric chain and (c) packing diagram	110
Fig. 3.18. ORTEP view and packing diagram of $[Pd\{CH\{P(C_7H_6)(p-$ $tolyl)_2\}COCH_3\}ClP(p-tolyl)_3]$ (23)	116
Fig. 3.19. Variable temperature ^{31}P NMR study on 18 (*, impurity)	121
Fig 3.20. ^{31}P NMR study on 21 in different concentrations, using DMSO as solvent. The concentration is increased in the order of $a < b < c < d < e$ (*, impurity)	122
Fig. 4.1. The optimized cis and trans structures for 1-3	142
Fig. 4.2. The optimized cis and trans structures for 4-6	143
Fig. 4.3. The optimized cis and trans structures for 7-9	144
Fig. 4.4. The optimized structure of compounds 10-12	150
Fig. 4.5. The optimized structure of compounds 13-15	151
Fig. 4.6. Calculated molecular structures of 7; (a), C-coordinated and (b), O- coordinated isomer	155

List of appendixes

2.1. IR spectrum of [Ph ₃ PCH ₂ COC ₆ H ₄ Cl]Br (1) (KBr disk)	160
2.2. ¹ H NMR spectrum of [Ph ₃ PCH ₂ COC ₆ H ₄ Cl]Br (1) (CDCl ₃) at 25 °C (*, impurity)	160
2.3. ³¹ P NMR spectrum of [Ph ₃ PCH ₂ COC ₆ H ₄ Cl]Br (1) (CDCl ₃) at 25 °C	161
2.4. ¹³ C NMR spectrum of [Ph ₃ PCH ₂ COC ₆ H ₄ Cl]Br (1) (CDCl ₃) at 25 °C (*, impurity)	161
2.5. IR spectrum of Ph ₃ PCHCOC ₆ H ₄ Cl (2) (KBr disk)	162
2.6. ¹ H NMR spectrum of Ph ₃ PCHCOC ₆ H ₄ Cl (2) (CDCl ₃) at 25 °C (*, impurity)	162
2.7. ³¹ P NMR spectrum of Ph ₃ PCHCOC ₆ H ₄ Cl (2) (CDCl ₃) at 25 °C	163
2.8. ¹³ C NMR spectrum of Ph ₃ PCH ₂ COC ₆ H ₄ Cl (2) (CDCl ₃) at 25 °C (*, impurity)	163
2.9. IR spectrum of [(<i>p</i> -tolyl) ₃ PCH ₂ COC ₆ H ₄ Cl]Br (3) (KBr disk)	164
2.10. ¹ H NMR spectrum of [(<i>p</i> -tolyl) ₃ PCH ₂ COC ₆ H ₄ Cl]Br (3) (CDCl ₃) at 25 °C	164
2.11. ³¹ P NMR spectrum of [(<i>p</i> -tolyl) ₃ PCH ₂ COC ₆ H ₄ Cl]Br (3) (CDCl ₃) at 25 °C	165
2.12. ¹³ C NMR spectrum of [(<i>p</i> -tolyl) ₃ PCH ₂ COC ₆ H ₄ Cl]Br (3) (CDCl ₃) at 25 °C	165
2.13. IR spectrum of [(<i>p</i> -tolyl) ₃ PCHCOC ₆ H ₄ Cl] (4) (KBr disk)	166
2.14. ¹ H NMR spectrum of [(<i>p</i> -tolyl) ₃ PCHCOC ₆ H ₄ Cl] (4) (CDCl ₃) at 25 °C	166
2.15. ³¹ P NMR spectrum of [(<i>p</i> -tolyl) ₃ PCHCOC ₆ H ₄ Cl] (4) (CDCl ₃) at 25 °C	167
2.16. ¹³ C NMR spectrum of [(<i>p</i> -tolyl) ₃ PCHCOC ₆ H ₄ Cl] (4) (CDCl ₃) at 25 °C	167
2.17. IR spectrum of [Ph ₃ PCH ₂ COC ₆ H ₄ NO ₂]Br (5) (KBr disk)	168
2.18. ¹ H NMR spectrum of [Ph ₃ PCH ₂ COC ₆ H ₄ NO ₂]Br (5) (CDCl ₃) at 25 °C (*, impurity)	168
2.19. ³¹ P NMR spectrum of [Ph ₃ PCH ₂ COC ₆ H ₄ NO ₂]Br (5) (CDCl ₃) at 25 °C	169
2.20. ¹³ C NMR spectrum of [Ph ₃ PCH ₂ COC ₆ H ₄ NO ₂]Br (5) (CDCl ₃) at 25 °C	169
2.21. IR spectrum of Ph ₃ PCHCOC ₆ H ₄ NO ₂ (6) (KBr disk)	170
2.22. ¹ H NMR spectrum of Ph ₃ PCHCOC ₆ H ₄ NO ₂ (6) (CDCl ₃) at 25 °C (*, impurity)	170
2.23. ³¹ P NMR spectrum of Ph ₃ PCHCOC ₆ H ₄ NO ₂ (6) (CDCl ₃) at 25 °C	171
2.24. ¹³ C NMR spectrum of Ph ₃ PCHCOC ₆ H ₄ NO ₂ (6) (CDCl ₃) at 25 °C	171
2.25. IR spectrum of [(<i>p</i> -tolyl) ₃ PCH ₂ COC ₆ H ₄ NO ₂]Br (7) (KBr disk)	172
2.26. ¹ H NMR spectrum of [(<i>p</i> -tolyl) ₃ PCH ₂ COC ₆ H ₄ NO ₂]Br (7) (CDCl ₃) at 25 °C (*, impurity)	172
2.27. ³¹ P NMR spectrum of [(<i>p</i> -tolyl) ₃ PCH ₂ COC ₆ H ₄ NO ₂]Br (7) (CDCl ₃) at 25 °C	173
2.28. ¹³ C NMR spectrum of [(<i>p</i> -tolyl) ₃ PCH ₂ COC ₆ H ₄ NO ₂]Br (7) (CDCl ₃) at 25 °C	173
2.29. IR spectrum of [(<i>p</i> -tolyl) ₃ PCHCOC ₆ H ₄ NO ₂] (8) (KBr disk)	174
2.30. ¹ H NMR spectrum of [(<i>p</i> -tolyl) ₃ PCHCOC ₆ H ₄ NO ₂] (8) (CDCl ₃) at 25 °C	174

2.31.	³¹ P NMR spectrum of [(<i>p</i> -tolyl) ₃ PCHCOC ₆ H ₄ NO ₂] (8) (CDCl ₃) at 25 °C	175
2.32.	¹³ C NMR spectrum of [(<i>p</i> -tolyl) ₃ PCHCOC ₆ H ₄ NO ₂] (8) (CDCl ₃) at 25 °C	175
2.33.	IR spectrum of 6a (KBr disk)	176
2.34.	¹ H NMR spectrum of 6a (CDCl ₃) at 25 °C (*, impurity)	176
2.35.	³¹ P NMR spectrum of 6a (CDCl ₃) at 25 °C	177
2.36.	¹³ C NMR spectrum of 6a (CDCl ₃) at 25 °C	177
2.37.	IR spectrum of 6b (KBr disk)	178
2.38.	¹ H NMR spectrum of 6b (CDCl ₃) at 25 °C (*, impurity)	178
2.39.	³¹ P NMR spectrum of 6b (CDCl ₃) at 25 °C	179
2.40.	¹³ C NMR spectrum of 6b (CDCl ₃) at 25 °C	179
2.41.	IR spectrum of 6c (KBr disk)	180
2.42.	¹ H NMR spectrum of 6c (CDCl ₃) at 25 °C (*, impurity)	180
2.43.	³¹ P NMR spectrum of 6c (CDCl ₃) at 25 °C	181
2.44.	¹³ C NMR spectrum of 6c (CDCl ₃) at 25 °C	181
2.45.	IR spectrum of 6d (KBr disk)	182
2.46.	¹ H NMR spectrum of 6d (CDCl ₃) at 25 °C	182
2.47.	³¹ P NMR spectrum of 6d (CDCl ₃) at 25 °C	183
2.48.	¹³ C NMR spectrum of 6d (CDCl ₃) at 25 °C	183
2.49.	IR spectrum of 6e (KBr disk)	184
2.50.	¹ H NMR spectrum of 6e (CDCl ₃) at 25 °C (*, impurity)	184
2.51.	³¹ P NMR spectrum of 6e (CDCl ₃) at 25 °C	185
2.52.	¹³ C NMR spectrum of 6e (CDCl ₃) at 25 °C	185
2.53.	IR spectrum of 6f (KBr disk)	186
2.54.	¹ H NMR spectrum of 6f (CDCl ₃) at 25 °C	186
2.55.	³¹ P NMR spectrum of 6f (CDCl ₃) at 25 °C	187
2.56.	¹³ C NMR spectrum of 6f (CDCl ₃) at 25 °C	187
2.57.	IR spectrum of 6g (KBr disk)	188
2.58.	¹ H NMR spectrum of 6g (CDCl ₃) at 25 °C (*, impurity)	188
2.59.	³¹ P NMR spectrum of 6g (CDCl ₃) at 25 °C	189
2.60.	¹³ C NMR spectrum of 6g (CDCl ₃) at 25 °C	189
2.61.	IR spectrum of 6h (KBr disk)	190
2.62.	¹ H NMR spectrum of 6h (CDCl ₃) at 25 °C	190

2.63. ^{31}P NMR spectrum of 6h (CDCl_3) at 25 °C	191
2.64. ^{13}C NMR spectrum of 6h (CDCl_3) at 25 °C	191
3.1. IR spectrum of $[(\text{Y}^1)\cdot\text{HgCl}_2]_2$ (KBr disk)	192
3.2. ^1H NMR spectrum of $[(\text{Y}^1)\cdot\text{HgCl}_2]_2$ ($\text{DMSO}-d_6$) at 25 °C (*, solvent impurity)	192
3.3. ^{31}P NMR spectrum of $[(\text{Y}^1)\cdot\text{HgCl}_2]_2$ ($\text{DMSO}-d_6$) at 25 °C	193
3.4. ^{13}C NMR spectrum of $[(\text{Y}^1)\cdot\text{HgCl}_2]_2$ ($\text{DMSO}-d_6$) at 25 °C	193
3.5. IR spectrum of $[(\text{Y}^1)\cdot\text{HgBr}_2]_2$ (KBr disk)	194
3.6. ^1H NMR spectrum of $[(\text{Y}^1)\cdot\text{HgBr}_2]_2$ ($\text{DMSO}-d_6$) at 25 °C (*, solvent impurity)	194
3.7. ^{31}P NMR spectrum of $[(\text{Y}^1)\cdot\text{HgBr}_2]_2$ ($\text{DMSO}-d_6$) at 25 °C	195
3.8. ^{13}C NMR spectrum of $[(\text{Y}^1)\cdot\text{HgBr}_2]_2$ ($\text{DMSO}-d_6$) at 25 °C	195
3.9. IR spectrum of $[(\text{Y}^1)\cdot\text{HgI}_2]_2$ (KBr disk)	196
3.10. ^1H NMR spectrum of $[(\text{Y}^1)\cdot\text{HgI}_2]_2$ ($\text{DMSO}-d_6$) at 25 °C (*, solvent impurity)	196
3.11. ^{31}P NMR spectrum of $[(\text{Y}^1)\cdot\text{HgI}_2]_2$ ($\text{DMSO}-d_6$) at 25 °C	197
3.12. ^{13}C NMR spectrum of $[(\text{Y}^1)\cdot\text{HgI}_2]_2$ ($\text{DMSO}-d_6$) at 25 °C	197
3.13. IR spectrum of $[(\text{Y}^2)\cdot\text{HgCl}_2]_2$ (KBr disk)	198
3.14. ^1H NMR spectrum of $[(\text{Y}^2)\cdot\text{HgCl}_2]_2$ (CDCl_3) at 25 °C (*, solvent impurity)	198
3.15. ^{31}P NMR spectrum of $[(\text{Y}^2)\cdot\text{HgCl}_2]_2$ (CDCl_3) at 25 °C	199
3.16. ^{13}C NMR spectrum of $[(\text{Y}^2)\cdot\text{HgCl}_2]_2$ ($\text{DMSO}-d_6$) at 25 °C	199
3.17. IR spectrum of $[(\text{Y}^2)\cdot\text{HgBr}_2]_2$ (KBr disk)	200
3.18. ^1H NMR spectrum of $[(\text{Y}^2)\cdot\text{HgBr}_2]_2$ (CDCl_3) at 25 °C	200
3.19. ^{31}P NMR spectrum of $[(\text{Y}^2)\cdot\text{HgBr}_2]_2$ (CDCl_3) at 25 °C	201
3.20. ^{13}C NMR spectrum of $[(\text{Y}^2)\cdot\text{HgBr}_2]_2$ (CDCl_3) at 25 °C	201
3.21. IR spectrum of $[(\text{Y}^2)\cdot\text{HgI}_2]_2$ (KBr disk)	202
3.22. ^1H NMR spectrum of $[(\text{Y}^2)\cdot\text{HgI}_2]_2$ (CDCl_3) at 25 °C	202
3.23. ^{31}P NMR spectrum of $[(\text{Y}^2)\cdot\text{HgI}_2]_2$ (CDCl_3) at 25 °C	203
3.24. ^{13}C NMR spectrum of $[(\text{Y}^2)\cdot\text{HgI}_2]_2$ ($\text{DMSO}-d_6$) at 25 °C	203
3.25. IR spectrum of $[(\text{Y}^3)\cdot\text{HgCl}_2]_2$ (KBr disk)	204
3.26. ^1H NMR spectrum of $[(\text{Y}^3)\cdot\text{HgCl}_2]_2$ ($\text{DMSO}-d_6$) at 25 °C (*, solvent impurity)	204
3.27. ^{31}P NMR spectrum of $[(\text{Y}^3)\cdot\text{HgCl}_2]_2$ ($\text{DMSO}-d_6$) at 25 °C	205
3.28. ^{13}C NMR spectrum of $[(\text{Y}^3)\cdot\text{HgCl}_2]_2$ ($\text{DMSO}-d_6$) at 25 °C	205
3.29. IR spectrum of $[(\text{Y}^3)\cdot\text{HgBr}_2]_2$ (KBr disk)	206
3.30. ^1H NMR spectrum of $[(\text{Y}^3)\cdot\text{HgBr}_2]_2$ ($\text{DMSO}-d_6$) at 25 °C (*, solvent impurity)	206