

Pyridylphosphines

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George R. Newkome is currently Vice President for Research and Distinguished Research Professor of Chemistry at the University of South Florida. Dr. Newkome has published over 250 papers in international journals and numerous books in the areas of organic and organometallic chemistry. He is a Fellow of the American Association for the Advancement of Science and a recent recipient of the Florida Award of the Florida Section of the American Chemical Society.

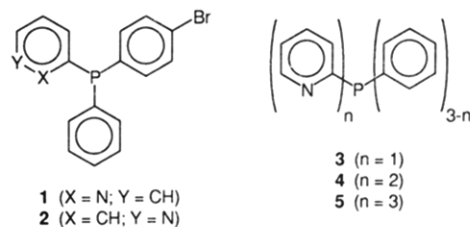
I. Introduction

The general preparation of phosphines has recently been overviewed¹ by Gilheany and Mitchell; however, their excellent review contained only two references (out of 394) that specifically addressed the area of pyridylphosphines. Their review should be the starting point with the following presentation being considered an addendum which covers the novel synthetic problems, reactions, and catalytic properties as well as lists the known metal complexes of the pyridylphosphines. It is hoped that this review will open new synthetic thoughts toward unique *P*- and *N*-ligands as well as to other combinations affording novel and useful complexes. In view of the increasing usage of pyridylphosphines in metal ion coordination through the 1980s, coupled with their novel fragmentation and derivatization, this field will continue to expand as new structural combinations are prepared.

II. General Synthetic Methods

The first reported preparation of a pyridylphosphine was presented² in 1944 by Davies and Mann as part of a study on the optical resolution of tertiary phosphines. Pyridylmagnesium bromide, initially generated via the entrainment process,³ was treated with phenyl(4-bromophenyl)chlorophosphine to afford (5%) the first pyridylphosphine 1 (Scheme 1). Interestingly, when 3-pyridylmagnesium bromide was reacted similarly² the only known, to the best of my knowledge,⁴ 3-pyridylphosphine 2 was prepared in a poor 7% yield.

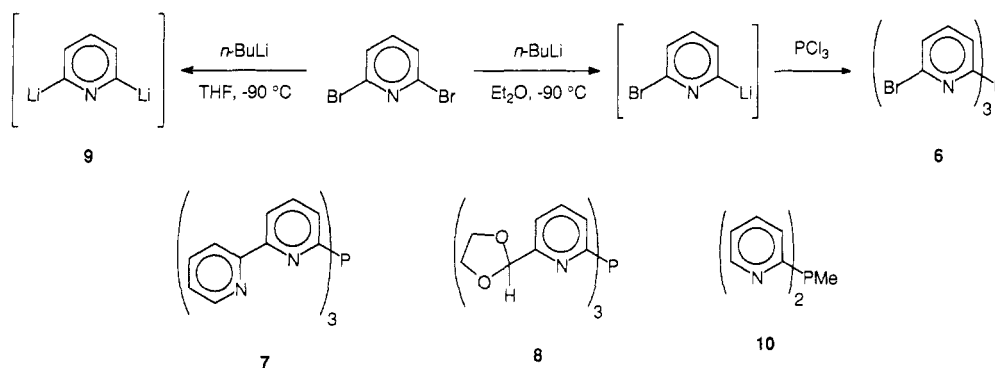
Scheme 1



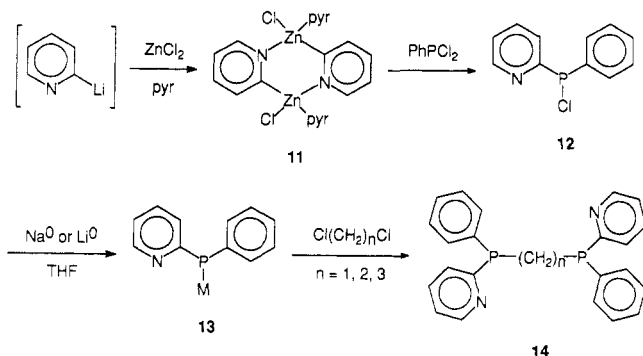
The tri-2-pyridylphosphine (5) was prepared (13%) from 2-pyridylmagnesium bromide with PCl_3 , whereas in 1948, this procedure was extended⁵ to the synthesis of 3 and 4. Numerous modifications of this general approach have appeared^{6,7,9,156} utilizing the corresponding 2-lithiopyridine with PCl_3 at lower (-65 to -100 °C) temperatures to afford 5 in improved (66%)¹⁵⁶ yields. Care must be taken to ensure complete formation of pyridyllithiums prior to the addition of the phosphorus halide^{7,8} since using traditional lithium-bromine exchange⁹ procedures followed by addition of PBr_3 generally gave rise to a mixture of di-2-pyridylbutylphosphine and dipyridine.

In a benchmark series of papers,¹⁰⁻¹³ Holm et al. established the optimum conditions for the use of pyridyllithiums in the synthesis of pyridylphosphines as well as a variety of related ligands incorporating pyridine rings. Very low temperatures (-65 to -100 °C) were shown to be essential, depending on the specific bromopyridine, in order to ensure pyridyllithium formation.^{14,15} An outstanding example demonstrating this procedure is the selective preparation of 6-bromo-

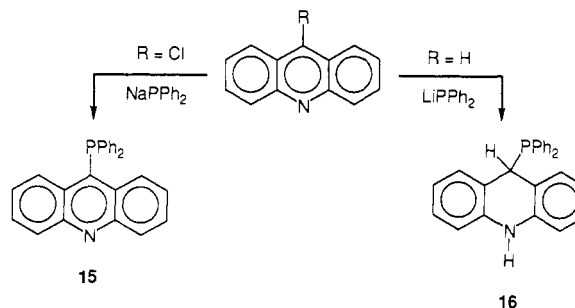
Scheme 2



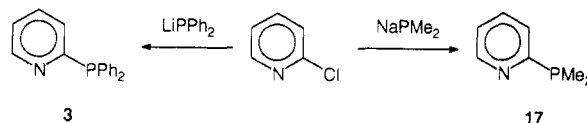
Scheme 3



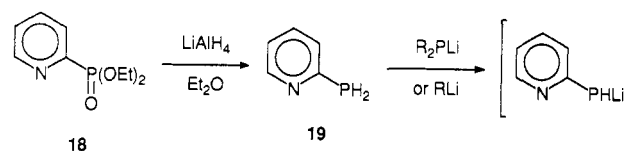
Scheme 4



Scheme 5



Scheme 6



2-lithiopyridine and its subsequent conversion (75%) at -90 °C to the tris(6-bromo-2-pyridyl)phosphine (6, Scheme 2).¹² Phosphines 7 and 8 were prepared¹² by reaction of the appropriate pyridyllithium with PCl₃ in 17% and 40% yields, respectively. Their conversion of acetal 8 to the corresponding oxime eventually afforded novel entrance to three-dimensional macrocycles capable of metal ion encapsulation. As a synthetic sidenote the use of diethyl ether permitted selective formation of the monolithiated bromopyridine; whereas with THF, 2,6-dilithiopyridine (9) was generated.¹⁶

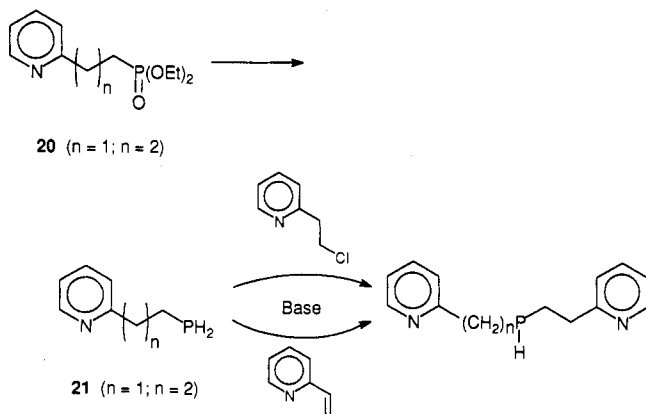
The addition of 2-lithiopyridine to several chlorophosphines was later repeated¹⁷ to generate 3 (44%), 4 (39%), and 5 (20%). Diphenyl-4-pyridylphosphine was similarly prepared⁸¹ (39%) by the reaction of 4-lithiopyridine with chlorodiphenylphosphine. The alkyl 2-pyridylphosphine 10 was prepared (43%) by using methyl dichlorophosphine.¹⁸ Bis(pyridylphosphines) were prepared¹⁹ from 2-lithiopyridine via its conversion to the novel zinc intermediate 11, which upon the addition of phenyldichlorophosphine at -20 °C was transformed (50% overall) to the chloro-2-pyridylphenylphosphine (12) (Scheme 3). Subsequent reduction of 12 with Na⁰ ("is capricious and may take from a few hours to several weeks...")¹⁹ afforded the corresponding phosphide 13, which on addition of an dichloroalkane gave a series of bis-*P,N*-ligands 14. The use of activated Li⁰ in this reduction is quicker but gives rise to less pure products.

In 1965, direct nucleophilic substitution by phosphide on pyridine occurred²⁰ since when 9-chloroacridine was treated with KP(C₆H₅)₂ in dioxane, phosphine 15 resulted (48%); whereas, when unsubstituted acridine was treated with LiP(C₆H₅)₂, the dihydro derivative 16 was formed in 31% yield (Scheme 4).

This general procedure was extended²¹ to numerous halopyridines; the 2- and 4-derivatives were reactive under the reaction conditions, and the 3-halopyridines were inert. Later, Balch et al.²² reported that the similar treatment of 2-chloropyridine with LiP(C₆H₅)₂, generated from diphenylphosphine with butyllithium in THF at 20 °C, gave excellent (94%) yields of 3. Modification²³ of this procedure and the analogous reaction with NaP(C₆H₅)₂ have been reported;²⁴ whereas with NaP(CH₃)₂, 17 has been formed (62%)¹⁸ (Scheme 5). When McFarlane et al.^{25,26} treated 2,6-difluoropyridine with NaP(C₆H₅)₂ in liquid ammonia, a convenient one-pot procedure of 2,6-bis(diphenylphosphino)pyridine was realized (40%). 6,6'-Dibromo-2,2'-dipyridine was smoothly transformed (65%) with LiP(C₆H₅)₂ to the corresponding bis-phosphine; subsequent oxidation with hydrogen peroxide afforded (89%) the bis-*P*-oxide.²¹

Reduction of diethyl 2-pyridylphosphonate (18)^{27,28} with LiAlH₄ gave (ca. 80%) the related 2-pyridylphosphine (19)²⁹ (Scheme 6). Selective abstraction of protons from 19 and/or (C₆H₅)PH₂ or (C₆H₅)₂PH offers interesting opportunities to prepare novel *P*-ligands, since 19 is a stronger P-H acid than the other two. The lithio 2-pyridyl phosphide was smoothly converted into

Scheme 7



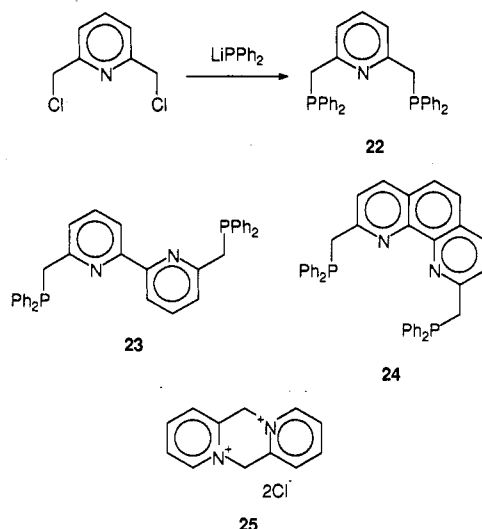
useful mono- and bidentates, and it readily, but reversibly, undergoes a Michael addition to α,β -unsaturated esters, including dimethyl vinylphosphonate. This reduction of pyridylphosphonates with LiAlH_4 should be applicable to other interesting esters, such as diethyl 4-pyridylphosphonate,³⁰ dimethyl [(4'-methyl-2,2'-bipyridin-4-yl)methyl]phosphonate,³¹ (3- and 4-phosphonoalkyl)pyridine derivatives,³² 2,6-pyridinyl methylphosphonates,³³ and (pyridylamino)methyl-(phosphonoalkyl)phosphinates.^{34,35}

The related (pyridylalkyl)phosphines were prepared³⁶ by reduction of phosphonates **20**^{37,38,39,40,41} with LiAlH_4 to afford (64%) **21** ($n = 2$) (Scheme 7). Nucleophilic addition of lithio or sodio phosphides (e.g. **21**, $n = 2$) to 2-vinylpyridine gave access to mono- and dialkylphosphines (refs 42, 43 and 36, 44, respectively). A modification of the Uhlig and Maaser procedure⁴² for 2-pyr(CH_2)₂ $\text{P}(\text{C}_6\text{H}_5)_2$ was recently presented;⁴⁵ however, the advantages were not obvious. DuBois et al. reported⁷⁶ the free-radical addition of phenylphosphine to 2-vinylpyridine in the presence of AIBN under irradiation to afford [2-pyr(CH_2)₂]₂ $\text{P}(\text{C}_6\text{H}_5)_2$, as a useful tridentate ligand. Similarly, treatment of 2,6-pyridinedimethanol with sodium hydride followed by allyl chloride afforded a diallyl ether, which, when irradiated in benzene in the presence of AIBN and excess $(\text{C}_6\text{H}_5)_2\text{PH}$, gave (91%) 2,6-pyr[$\text{CH}_2\text{O}(\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2$]₂.⁴⁶

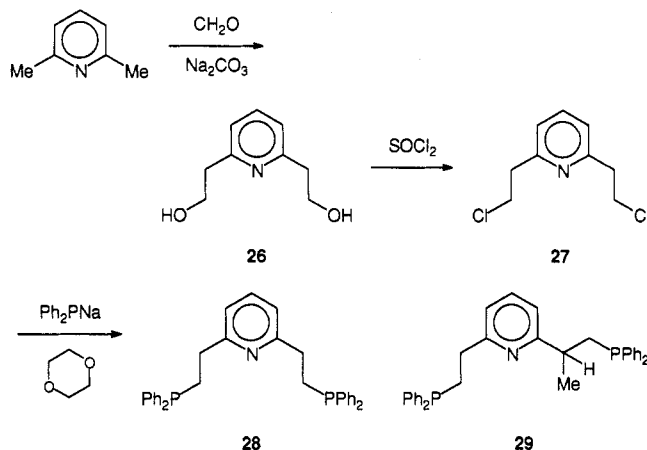
Simple nucleophilic substitution⁴⁷ of α -chloromethylheteroaryls with lithio or potassio diphenylphosphide (ref 48 and 49, respectively) under strictly air-free conditions has been shown to give variable yields (54–94%) of diverse pyridines **22** and **23** as well as pyridine-related bisphosphines (**24**) (Scheme 8). Spiegel and Stetzer reported³⁶ that 2-(chloromethyl)pyridine dimerized to give 6,12-dihydrodipyrido[1,2- α :1',2'- d]pyrazinediylum dichloride (**25**), which with $\text{LiP}(\text{C}_6\text{H}_5)_2$ gave the known⁵⁰ dipyrido[1,2- α :1',2'- d]pyrazine. However when 2-(chloromethyl)pyridine was treated with $\text{C}_6\text{H}_5\text{PHNa}$ in THF at -78°C exchange occurred to afford (74%) 2-pyr $\text{CH}_2\text{PH}(\text{C}_6\text{H}_5)$; whereas using $\text{C}_6\text{H}_5\text{PHLi}$, (2-pyr CH_2)₂ was formed.³⁶

2,6-Bis[2-(diphenylphosphino)ethyl]pyridine (**28**) was prepared⁵¹ in three steps from lutidine utilizing a combination of known procedures (Scheme 9). 2,6-Lutidine was converted (8%) to the desired 2,6-bis(2-hydroxyethyl)pyridine (**26**) along with a mixture of related alcohols, via the method of Löffler and Theil.⁵² Conversion of (impure) **26** to the corresponding chloride **27** was conducted (50%) by treatment with thionyl

Scheme 8



Scheme 9



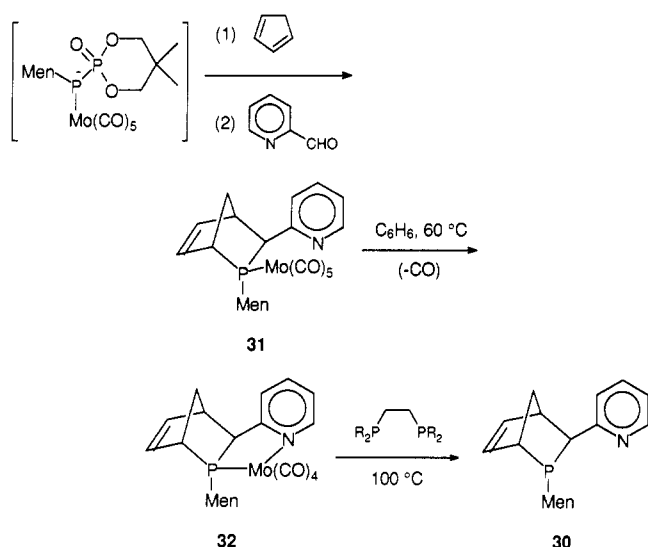
chloride. By using the general procedure of Issleib,⁵³ **27** with $\text{NaP}(\text{C}_6\text{H}_5)_2$ was transformed (23.8%) to the symmetrical diphosphine **28**. Also isolated was the unsymmetrical **29**, which was derived from the original impurities in starting material **27**.

Recently, an approach to chiral pyridylphosphine ligand **30** has been reported.⁵⁴ Complex **31** was prepared from the phospho-Wittig reagent, but it readily loses CO to form the stable chelate **32**. Decomplexation of **32** by treatment with DIPHOS at 100°C afforded **30** (Scheme 10); the retention of stereochemistry is proposed but not yet established.

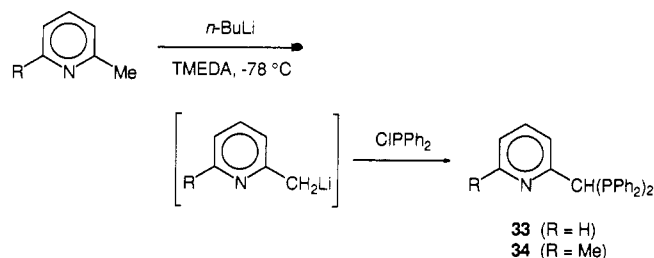
The use of the Arbuzov reaction to prepare phosphinoacetonitriles⁵⁵ has been recently applied to the synthesis of (pyridylalkyl)dialkylphosphines.^{56,57} Although LiAlH_4 can be used in the reduction of the pyridylphosphoryl intermediates, silanes are recommended in this procedure when sensitive functionality is to be retained.^{55,58}

The preparation of 2-[bis(diphenylphosphino)methyl]pyridine (**33**) was reported,⁵⁹ but the preferred method of synthesis⁶⁰ of **33** was by the generation of 2-(lithiomethyl)pyridine at -78°C and subsequent addition to $(\text{C}_6\text{H}_5)_2\text{PCl}$ (Scheme 11). The related 2-[bis(diphenylphosphino)methyl]-6-methylpyridine (**34**) was prepared^{61,62} in a similar manner. Treatment of 3-ethyl-4-methylpyridine or 9-methyloctahydroacridine with n -butyllithium, followed by $(\text{C}_6\text{H}_5)_2\text{PCl}$ and subsequent

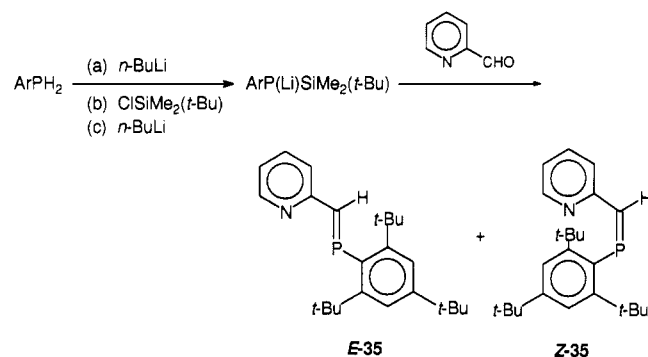
Scheme 10



Scheme 11



Scheme 12



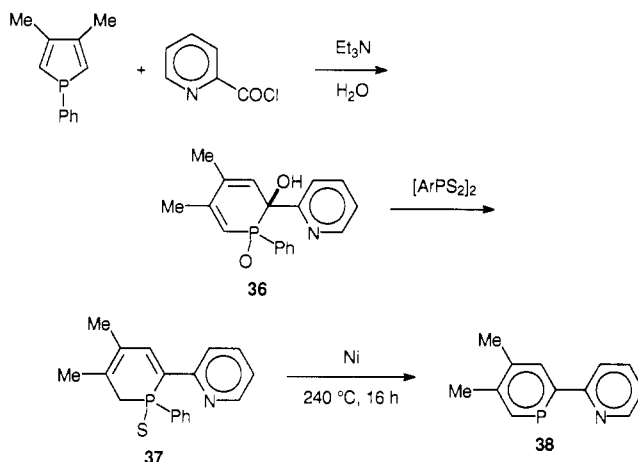
oxidation afforded low yields (ca. 21–26%) of the corresponding 4-substituted *P*-oxides.⁶³

Pyridylphosphaalkenes⁶⁴ (35) were prepared from the appropriate pyridinecarboxaldehyde and $\text{ArP}(\text{Li})\text{SiMe}_2\text{t-Bu}$, where Ar is 2,4,6-tri-*tert*-butylphenyl, via the procedure of Yoshifuji et al.^{65,66} (Scheme 12). These phosphorin 35s exist as *E*- and *Z*-isomers, can be separated by chromatography, are air stable, and can be stored for weeks at -25°C .

Synthesis of the first known phosphorus analogue of 2,2'-bipyridyl, 2-(2-pyridyl)-4,5-dimethylphosphorin (NIPHOS; 38), was reported by Mathey et al.⁶⁷ Initially 1-phenyl-3,4-dimethylphosphole was treated with picolinic acid chloride to give *P*-oxide 36, which was transformed to the *P*-sulfide 37. Pyrolysis of 37 in the presence of nickel gave the desired phosphorin 38 (Scheme 13). In view of the notable $\text{p}K_a$ (5.25) for pyridine and the inability to measure a $\text{p}K_a$ for phosphorin, ligand 38 was shown to be monobasic.⁶⁸

Table 1 gives the ^{31}P NMR data for most of the known pyridylphosphines, and Table 2 presents the ^{31}P NMR

Scheme 13



spectral data for several lithiophosphide, which were key intermediates in several of the reaction sequences.

III. Reactions

A. *N*- and *P*-Derivatives

Typical *P*-derivatives of pyridylphosphines include oxides,^{5,7,80–84} sulfides,^{2,5,7,83} selenides,⁷ methides,^{17,18,80} and methylphosphonium salts.^{2,5,17,18} Pyridylphosphines were smoothly converted to the corresponding *P*-oxides with chloroamine-*T*⁵ or aqueous H_2O_2 ,^{5,80,84,85,153} whereas, the use of *m*-chloroperbenzoic acid or peracetic acid can result in both *P*- and *N*-oxidation.^{80,81,86} The preparation of *P*-sulfides^{2,5} or *P*-selenides^{7,87} was readily accomplished by melting the corresponding phosphine with molecular sulfur or selenium, respectively. Bisphosphine 39 in the presence of neat excess MeI afforded the trimethiodide 40, which loses 1 equiv of MeI on standing at room temperature or heating (80°C) for 3 h *in vacuo* giving the bis-*P,P*-methiodide 41.²⁵ Slow aerial oxidation of 39 occurred upon standing for several weeks to generate the *P,P*-dioxide (42), whereas with sulfur or selenium, it was converted stepwise to the mono-*P*-derivatives 43 and then bis-*P,P*-derivatives²⁵ 44 (Scheme 14).

Scheme 14

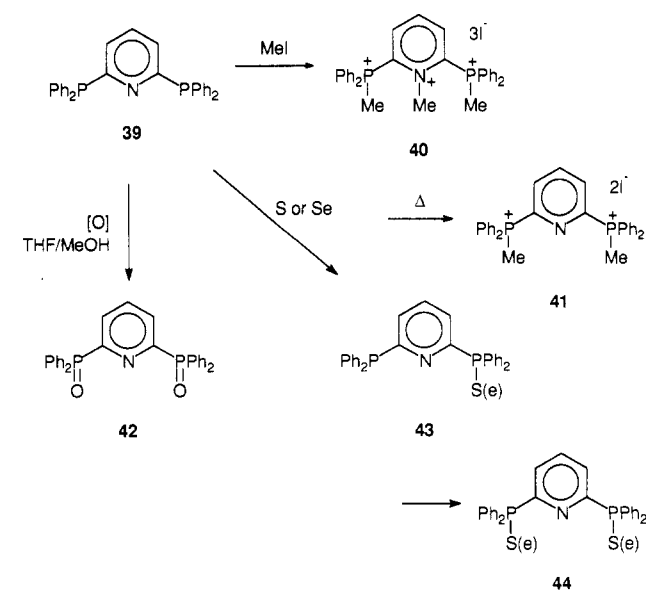


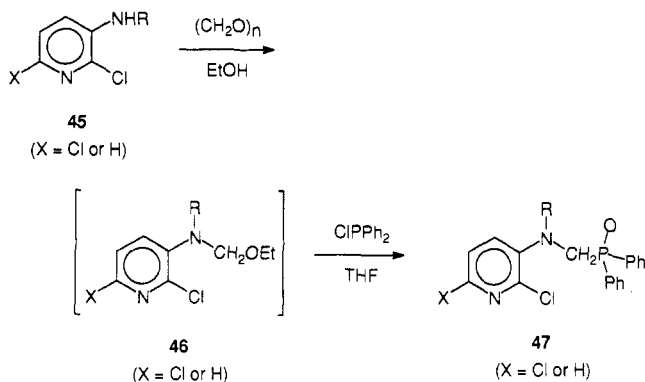
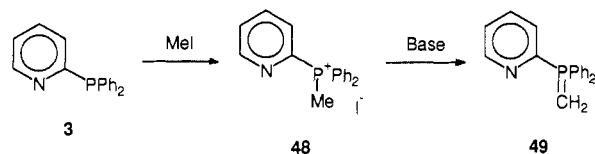
Table 1. ^{31}P NMR Data for the Ligands

pyridylphosphine	solvent	δ (ppm)	1J (PH)	ref(s)
2-pyrPH ₂		-121.4	203	29
2-pyrPHD		-124.3	204, 32 ($^1J_{\text{PD}}$)	29
2-pyrPD ₂		-127.0	32 ($^1J_{\text{PD}}$)	29
2-pyrPH(SiMe ₃)	<i>t</i> -BuOMe	-118.6	194	29
2-pyrP(SiMe ₃) ₂	<i>t</i> -BuOMe	-125.1		29
(2-pyrPH) ₂ CH ₂	DMF	-50.9, -54.8	223	29
2-pyrPHMe	DMF	-70.7	206	29
2-pyrPMe ₂	CH ₂ Cl ₂	20.6		29
	C ₆ D ₆	41.62		18
2-pyrPMe ₃ (I ⁻)	CF ₃ CO ₂ H	27.05		18
2-pyrPMe ₂ (=CH ₂)	CDCl ₃	5.69		18
(2-pyr) ₂ PMe	CDCl ₃	-19.82		18
(2-pyr) ₂ PMe ₂ (I ⁻)	CDCl ₃	17.59		18
(2-pyr) ₂ PMe(=CH ₂)	C ₆ D ₆ CD ₃	13.06		18
2-pyrPH ₂ $\cdot$ <i>N</i> -MeI	CH ₂ Cl ₂	-130.2	218	29
2-pyrPH ₂ $\cdot$ <i>N</i> -HCl	CH ₂ Cl ₂	-132.4	216	29
2-pyrPH(CMe ₂ CH ₂ COMe)	<i>t</i> -BuOMe	-9.0	215	29
2-pyrPH(CH ₂ CH ₂ CO ₂ Me)	<i>t</i> -BuOMe	-49.6	210	29
2-pyrPH(CH ₂ CHMeCO ₂ Me)	<i>t</i> -BuOMe	-57.1, -58.3	211, 210	29
2-pyrPHCH(C ₆ H ₅)CH ₂ CO ₂ Me	<i>t</i> -BuOMe	-23.3, 25.2	214, 210	29
2-pyrPH(CH ₂) ₂ PH ₂	<i>t</i> -BuOMe	-46.8, -128.8	209, 190	29
2-pyrP(C ₆ H ₅)OMe	CDCl ₃	110.2		69
2-pyrP(C ₆ H ₅) ₂ (3)	CD ₂ Cl ₂	-3.36		70
	CDCl ₃	-3.95		71
		-3.28		76, 111
		-2.7		70
		-4.03		23, 72
2-pyrP(O)(C ₆ H ₅) ₂ (<i>N</i> -O)	CDCl ₃	19.1		86
(2-pyr) ₂ P(C ₆ H ₅) (4)	CDCl ₃	-1.9		69
6,6''-(C ₆ H ₅) ₂ P(terp)P(C ₆ H ₅) ₂ ^a	CDCl ₃	-0.62		47
2-[6-(C ₆ H ₅) ₂ P(pyr)] ₂	CDCl ₃	-1.65		21, 47, 73
2-[6-(C ₆ H ₅) ₂ PCH ₂ (pyr)] ₂	CDCl ₃	-9.32		47
2,6-[(C ₆ H ₅) ₂ PCH ₂] ₂ (pyr)	CDCl ₃	-9.20		47
2-[(C ₆ H ₅) ₂ P](phen) ^b	CDCl ₃	-0.83		47
2,9-[(C ₆ H ₅) ₂ P] ₂ (phen) ^b	CDCl ₃	0.52		47
2,9-[(C ₆ H ₅) ₂ PCH ₂] ₂ (phen) ^b	CDCl ₃	-12.74		47
2,7-[(C ₆ H ₅) ₂ P] ₂ (naph) ^c	CDCl ₃	1.96		47
structure 30	C ₆ D ₆	9.06		54
2-pyr(CH ₂) ₂ PH ₂	neat	-142.1	192	36
2-pyr(CH ₂) ₂ PH(C ₆ H ₅)	neat	-53.7	208	36
		-52.4		74
2-pyr(CH ₂) ₂ P(C ₆ H ₅) ₂	CDCl ₃	-14.9		45
2-pyr(CH ₂) ₂ P(O)(C ₆ H ₅) ₂	CDCl ₃	31.5		45
[2-pyr(CH ₂) ₂ P(CCl ₂ H)(C ₆ H ₅) ₂]Cl	CDCl ₃	39.3		45
[2-pyr(CH ₂) ₂ P(CCl ₂ H)(C ₆ H ₅) ₂]Cl	CDCl ₃	30.7		45
[2-pyr(CH ₂) ₂ P(C ₆ H ₅) ₂ (OCH ₂ CHMe ₂)]Cl	CDCl ₃	73.1		45
2-pyr(CH ₂) ₂ PH(<i>t</i> -Bu)	neat	-26.5	189	36
2-pyr(CH ₂) ₂ PH(<i>i</i> -Pr)	neat	-38.3	192	36
2-pyrCH ₂ PH(C ₆ H ₅)	Et ₂ O	-48.0	209	36
2-pyrCHP(C ₆ H ₅) ₂ (OSiMe ₃)	C ₆ D ₆	2.8		36
2-pyrCHPH(C ₆ H ₅) ₂ (OSiMe ₃)	Et ₂ O	-21.2, -33.1	217, 211	36
2-pyr(CH ₂) ₂ P(SiMe ₃)	Et ₂ O	-154.1	186	36
2-pyr(CH ₂) ₂ P(C ₆ H ₅)SiMe ₃	Et ₂ O	-86.7		36
[2-pyr(CH ₂) ₂] ₂ PH	Et ₂ O	-70.9	199	36
[2-pyr(CH ₂) ₂] ₂ P(C ₆ H ₅)	THF	-24.4		36
	CDCl ₃	-24.4 ^d		75
2-(pyr) ₃ P (5)	CDCl ₃	-0.05		76, 84
[(C ₆ H ₅) ₂ (2-pyr)P] ₂ CH ₂	CDCl ₃	-19.2	>30 (J_{PP})	19
[(C ₆ H ₅) ₂ (2-pyr)PCH ₂] ₂	CDCl ₃	-10.4	≈35 (J_{PP})	19
[(C ₆ H ₅) ₂ (2-pyr)PCH ₂] ₂ CH ₂	CDCl ₃	-14.5	<1 (J_{PP})	19
2,6-[(C ₆ H ₅) ₂ P] ₂ pyr		-4.5		25
		-3.4		77
2,6-[(C ₆ H ₅) ₂ P(O)] ₂ pyr		19.8		25
		20.86		85
2,6-[(C ₆ H ₅) ₂ P(S)]pyr[P(C ₆ H ₅) ₂]		35.6, -2.6		25
2,6-[(C ₆ H ₅) ₂ P(S)] ₂ pyr		37.7		25
2,6-[(C ₆ H ₅) ₂ P(Se)]pyr[P(C ₆ H ₅) ₂]		30.8, -2.8	748 ($^1J_{\text{PSe}}$)	25
2,6-[(C ₆ H ₅) ₂ P(Se)] ₂ pyr		31.6	741 ($^1J_{\text{PSe}}$)	25
2,6-[(C ₆ H ₅) ₂ P(Me)] ₂ pyr [2I ⁻]		21.1		25
(5)-[N-CH(CH ₂)SO ₃ ⁻ (CH ₂) _n CH ₃]	D ₂ O	-22.52		78
<i>E</i> -(2-pyrCH=PAr)	CDCl ₃	285.41		64
<i>Z</i> -(2-pyrCH=PAr)	CDCl ₃	259.6		64
<i>E,E</i> -[2,6-pyr(CH=PAr) ₂]	CDCl ₃	283.01		64
<i>E,Z</i> -[2,6-pyr(CH=PAr) ₂]	CDCl ₃	281.51, 256.9		64
2,6-pyr[CH ₂ O(CH ₂) ₃ P(C ₆ H ₅) ₂]	CH ₂ Cl ₂	-15.9		46
structure 36	CDCl ₃	20.4		67
structure 37	CDCl ₃	23.4		67
NIPHOS ^e (38)	CDCl ₃	184.9		67
		187.8		79
NIPHOS-HCl ^e	CDCl ₃	196.6		68

^a Terp = 4'-phenyl-2,2':6',2''-terpyridine. ^b Phen = 1,10-phenanthroline. ^c Naph = 2,7-naphthyridine. ^d Calculated value δ = 22.0. ^e NIPHOS (38) = 2-(2-pyridyl)-4,5-dimethylphosphorine.

Table 2. ^{31}P NMR for the Lithiopyridylphosphines

lithiopyridylphosphines	solvent	δ (ppm)	1J (PH)	ref
2-pyrP HLi	<i>t</i> -BuOMe	-96.6	195	29
2-pyrP $\text{Li}(\text{SiMe}_3)$	<i>t</i> -BuOMe	-112.7		29
2-pyrCH $_2$ P $\text{Li}(\text{C}_6\text{H}_5)$	THF-Me	-46.9		36
2-pyr(CH $_2$) $_2$ P HLi	THF-Me	-162.2	155	36
2-pyr(CH $_2$) $_2$ P $\text{Li}(\text{C}_6\text{H}_5)$	THF-Me	-58.5		36
2-pyr(CH $_2$) $_2$ P $\text{Li}(t\text{-Bu})$	THF-Me	-27.3		36
2-pyr(CH $_2$) $_2$ P $\text{Li}(i\text{-Pr})$	THF-Me	-40.1		36

Scheme 15**Scheme 16**

Halogenated 3-[*N*-alkyl-*N*-[(diphenylphosphino)ethyl]amino]pyridines (47) were prepared (85–91%) by treatment of the intermediate *N,O*-acetals 46, generated from 3-(*N*-alkylamino)-2-chloro- or 2,6-dichloropyridines (45) via the Mannich reaction, with $(\text{C}_6\text{H}_5)_2\text{PCl}^{88}$ (Scheme 15).

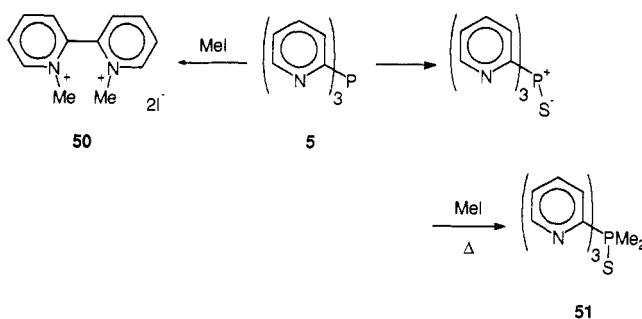
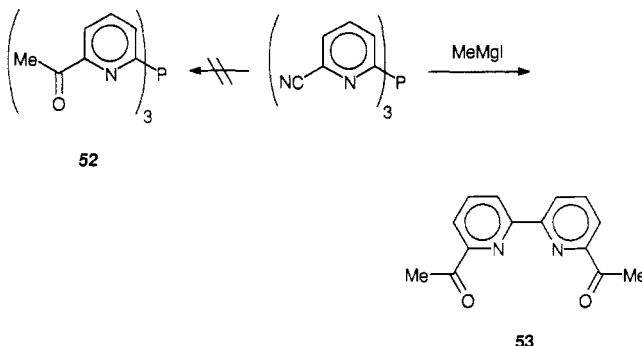
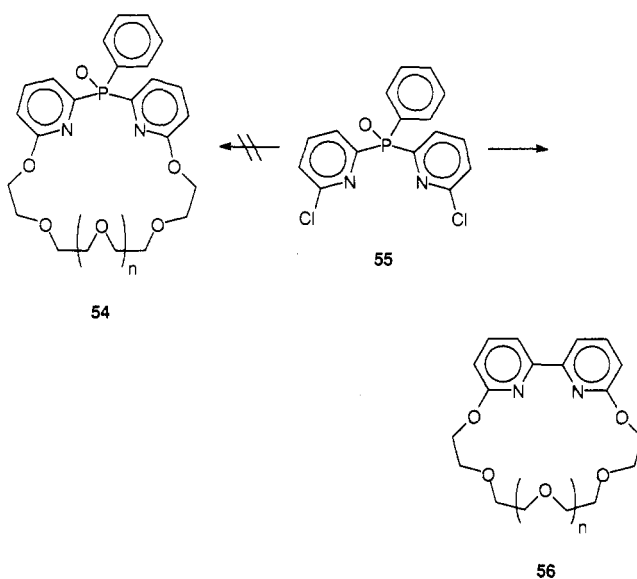
Formation of *P*-methyl pyridylphosphonium salts 48 was accomplished by treatment of the phosphine with cold methyl iodide.⁵ These salts can be readily converted to the *P*-methiodide 49 upon reaction with KH^{18} or trimethylphosphine methide¹⁷ (Scheme 16).

B. Fragmentation Reactions

Unusual fragmentations of pyridylphosphine derivatives were first noted² as early as 1944, when the *P*-sulfide of 3 was heated with methyl iodide and surprisingly only tetramethylphosphonium iodide was isolated. Later it was found⁵ that 5, when treated with methyl iodide at 100 °C afforded only 2,2'-dipyridine dimethyl iodide (50), whereas the *P*-sulfide of 5 gave phosphonium sulfide 51 under similar reaction conditions (Scheme 17). This fragmentation-recombination was initially rationalized by the formation of 2-pyridyl radicals, which subsequently recombined to afford the bipyridine products.

During his attempted synthesis of tris(6-acetylpyridinyl)phosphine (52), Parks¹⁴ discovered that addition of methylmagnesium iodide to the corresponding trisnitrile gave predominantly 6,6'-diacetyl-2,2'-dipyridine (53) via a similar expulsion process (Scheme 18).

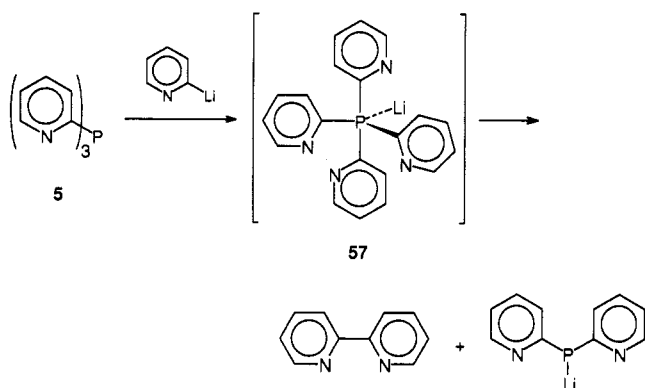
More recently during the preparation of pyridylphosphine macrocycles, Newkome and Hager⁸⁹ treated ligand 55 with alkoxide and isolated not the desired

Scheme 17**Scheme 18****Scheme 19**

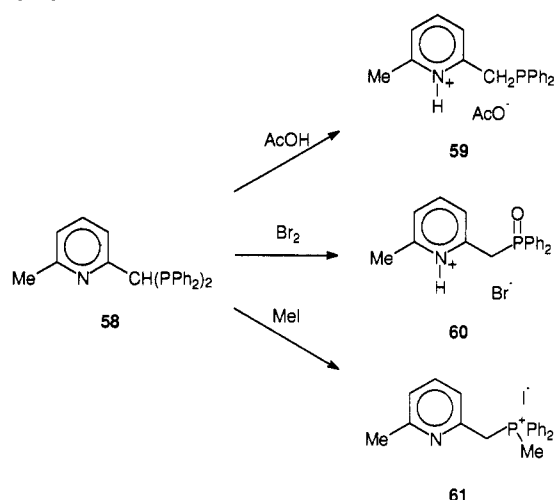
P-macrocyclic 54 but rather 56, which was free of phosphorus (Scheme 19). It was demonstrated⁸⁹ that *P*-oxides readily undergo a benzylic acid like rearrangement with the extrusion of a phosphorus moiety, whereas the parent phosphine of 55 was smoothly converted (47%) to the desired *P*-macrocyclic. Further treatment of *P*-oxide 55 with sodium glycolate at 90–100 °C in toluene afforded (32%) the ring-contracted 56. The proposed⁸⁹ benzylic acid type rearrangement is similar to that suggested below by Oae and Uchida. This extrusion was not limited to *P*-oxides but that also *S*-dioxides^{90,91} and dipyridyl ketones⁹² undergo a similar reaction under basic conditions.

Oae and co-workers^{93–95} have reexamined in detail this extrusion process in related examples. When 5 was heated with 2-pyridyllithium, 2,2'-dipyridine was

Scheme 20



Scheme 21



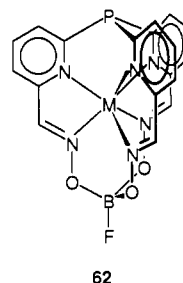
isolated in 81% yield. This transformation was rationalized as nucleophilic attack of the heteroaryllithium,⁹³ or more generally an organometallic⁹⁴ reagent on the phosphorus atom to generate a pentacoordinate intermediate 57, from which the equatorial group couples with the axial substituent to give the products (Scheme 20). Phosphonium salts and *P*-oxides possessing at least two 2-pyridyl groups, when treated with acid or neutral solvents,⁹⁵ gave the corresponding 2,2'-dipyridine. Oae and Uchida have recently reviewed⁹⁶ the ligand-coupling reactions of hypervalent species of which these transformations can be envisioned as but examples.

Bis-phosphines, e.g. 58, react with various reagents to give derivatives of 2-[(diphenylphosphino)methyl]pyridine.⁶² Treatment of 58 with acetic acid, bromine, or methyl iodide under diverse conditions gave 59, 60, or 61, respectively, with the loss of one of the *P*-moieties (Scheme 21). A rationale for these degradations was presented.⁶²

C. Metal Ion Coordination

It was nearly two decades before pyridylphosphines were first reported as ligands in metal ion complexation. In 1966, Uhlig and Maaser initially reported⁴² the preparation of Ni(II), Co(II), Zn(II), and Cu(I) complexes of 2-pyr(CH₂)₂P(C₆H₅)₂. They confirmed the structural assignments of these 1:1- and 1:2-complexes by conductivity, electronic spectra, and analytical data; since these were simple structures, these supportive data were marginally sufficient.

Scheme 22



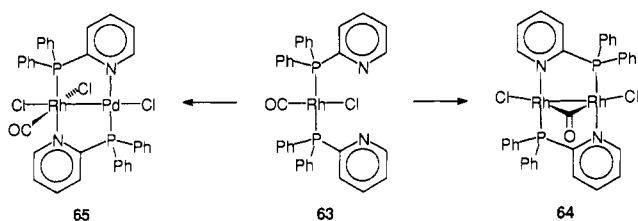
The first pivotal point in better understanding the complexation of pyridylphosphines was the rapid acquisition of X-ray crystallographic data. The earliest example was reported by Park, Wagner, and Holm in their 1970 communication,¹⁰ when they synthesized hexacoordinate complexes possessing nonoctahedral stereochemistry. Their three-dimensional macrocycles incorporated a substituted tri-2-pyridylphosphine moiety, which utilized the three directed pyridine *N*-electron pairs along with the corresponding juxtaposed oxime groups. These structures were supported by electronic spectra, infrared data, conductivity studies, ¹⁹F NMR spectroscopy, and analytical data. Although the synthetic methodology and these traditional supportive data strongly supported the assigned structures, it was footnoted that Churchill and Reis⁹⁷ had completed a single-crystal X-ray study of {Ni[P(2,6-pyrCH=NO)₃BF](BF₄)} (62, Scheme 22), thus confirming the unique solid state structure.

Holm et al.¹¹ elaborated on their initial studies of these "clathro chelate"⁹⁸ structures, and Churchill and Reis added the key X-ray data^{97,99,100} supporting the structures as well as revealing the structural solid-state subtleties, that were impossible to obtain from classical methods. Although these initial X-ray studies were directed mainly at the *N*-coordination of these complexes, it will be demonstrated that without X-ray data the full understanding of pyridylphosphine complexation would not have been possible.

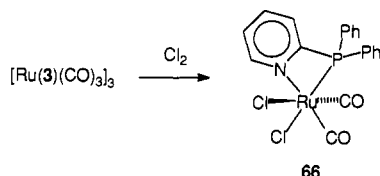
Throughout the 1970s, a few research groups utilized other simple pyridylphosphines to prepare various uncomplicated metal ion complexes, which were characterized by the application of the traditional techniques, such as IR,^{44,51,61,83,101-103} conductivity,^{51,61,83,101,102} molecular weight,^{51,61,102} magnetic susceptibility,^{43,61,101-103} electronic spectra,^{43,44,51,61,83,102,103} X-ray powder diffraction,⁵¹ and elemental analyses,^{43,44,51,61,83,101-103} as well as studies of their electrochemical properties.^{104,105}

The second major breakthrough in the chemistry of pyridylphosphines came when NMR spectral information became readily available for phosphorus (³¹P) and other metal centers (e.g., ¹⁹⁵Pt), thus permitting a quick snapshot of the *P*-center as well as diamagnetic metal center(s). This was especially true with the advent of di- and polynuclear metal complexes, bridged by *N,P*-ligands. In 1980, three groups^{8,74,121} initially utilized this spectral NMR technique to establish the foundation for the more complicated complexes to follow. Although the traditional spectral and analytical data were still acquired, the combination of ³¹P NMR and single-crystal X-ray analysis as the pivotal tools for most researchers in the field, opened the threshold to numerous new metallomacrocycles.

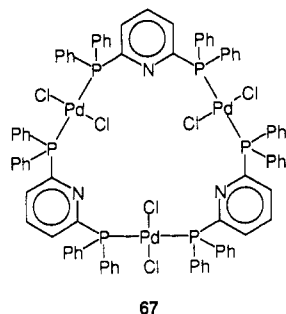
Scheme 23



Scheme 24



Scheme 25



With the growing interest in binuclear complexes,¹⁰⁶ Balch et al.¹¹⁰ found **3** to be a convenient building block to evaluate the stepwise introduction of similar and different metal atoms. Thus, the addition of $\text{Rh}_2(\mu\text{-Cl})(\text{CO})_4$ to **3** generated the P,P' -complex **63**, which with an additional equivalent of $\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4$ was converted to $\text{Rh}_2(3)_2(\mu\text{-CO})(\text{Cl}_2)$ (**64**), although with $\text{Pd}(\text{COD})\text{Cl}_2$ the binuclear complex **65** formed (Scheme 23). ^{31}P NMR and single-crystal X-ray data were primary spectral tools to establish these structures, as well as numerous related binuclear transition metal complexes.

Generally **3** acts as a P -monodentate ligand as noted by the initial generation of **63**; however, N -monodentate

coordination and P,N -chelation of a single metal ion are also possible. Addition of chlorine to $[\text{Ru}(3)(\text{CO})_3]_3$ was a convenient route to **66**, which possesses a strained, four-membered chelate ring and is a single isomer even though four geometrical isomers are possible⁷⁰ (Scheme 24).

The creation of polynuclear complexes was possible utilizing 2,6-bis(diphenylphosphino)pyridine (**39**), which with PdCl_2 readily formed the stable P -trimer **67**¹⁰⁸ (Scheme 25), suggesting possible limited structural flexibility. The addition of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ to **39**, however, gave rise to the dinuclear complex **68**¹⁴⁹ which with tin(II) chloride afforded **69**. This insertion of a central metal atom is quite rare due to the rigidity of the bridging ligand **68**. The attempted incorporation of a central rhodium ion by the addition of $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$ resulted in a cleavage-recombination of **68** to create the tetranuclear complex **70**, in which each ligand bridges three rhodium atoms and is stable in solution.¹⁰⁸

There appears to be a reversible molecular reorganization¹⁶⁰ of **69** to **70** in which two rhodium atoms have been eliminated; treatment of **70** with $\text{Rh}(\mu\text{-Cl})_2(\text{CO})_4$ regenerates **69** (Scheme 26).

It is beyond the scope of this review to discuss the myriad of polynuclear metal pyridylphosphines; however, relevant data for most of the known complexes that have been thoroughly characterized are summarized in Tables 3–8. Tables 3–7 present the key ^{31}P NMR results, as well as other pertinent data associated with the central metal atom(s); Table 8 presents a list of pertinent bond angles and distance from the known X-ray crystal studies yet conducted.

D. Catalytic Reactions with Pyridylphosphine Complexes

1. Formylation/Carbonylation Reactions

Although hydrogenation of alkenes using $\text{RhCl}[\text{5}]_2$, $\{\text{Rh}(\text{C}_6\text{H}_{12})[\text{5}]_2\}[\text{PF}_6]$, or $\text{RhHCl}[\text{5}]_3$ was unsuccessful, when excess **5** and low CO and hydrogen (1:1) pressures were used with $\text{RhH}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3][\text{5}]_2$, as catalyst

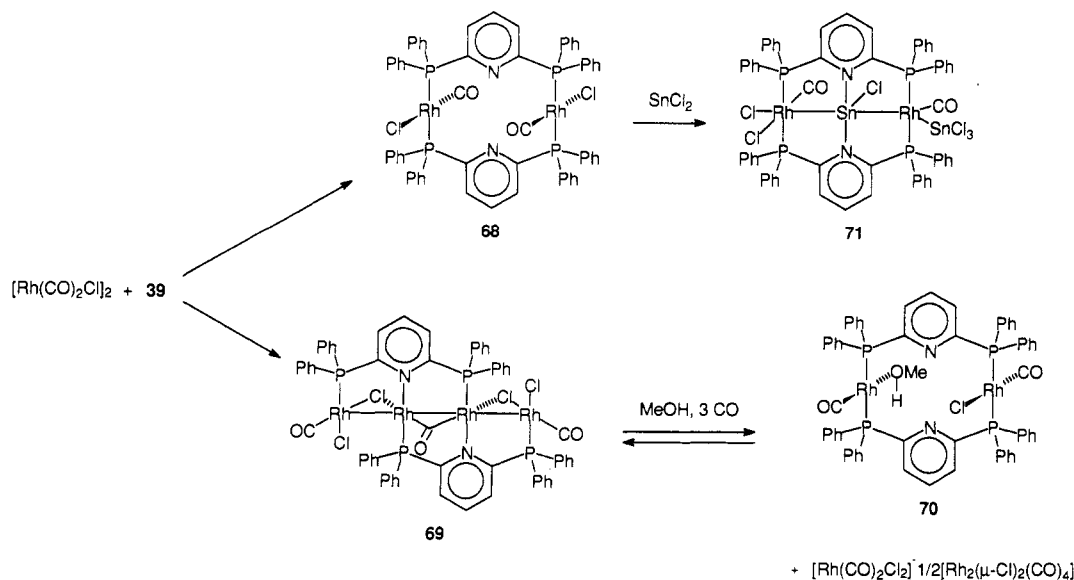


Table 3. ^{31}P NMR for the Palladium Pyridylphosphine Complexes

palladium complexes	solvent/temp (K)	δ (ppm)	3J (Hz)	ref(s)
$\text{Pd}(t\text{-BuNC})(3)\text{Cl}_2$	CDCl_3	24.5		107
$\text{Pd}(\text{CH}_2\text{CMeCH}_2)(3)\text{Cl}$	$\text{CDCl}_3/255$	24.3		107
$\text{cis-Pd}(\text{pyrH})(4)\text{Cl}_2$	$\text{DMSO}-d_6$	30.5		69
$\text{cis,cis,trans-Pd}_3\{\mu\text{-}[(\text{C}_6\text{H}_5)_2\text{P}]_2\text{pyr}\}_3\text{Br}_6$		36.4, 19.9, 14.7		77
$\text{cis,cis,trans-Pd}_3\{\mu\text{-}[(\text{C}_6\text{H}_5)_2\text{P}]_2\text{pyr}\}_3\text{Cl}_6$	CD_2Cl_2	37.8, 23.0, 17.1		108, 77
$\text{trans-Pd}(3)_2\text{Cl}_2$	CD_2Cl_2	23.8, 23.4		22, 109, 110
	CDCl_3	22.9		111
$\text{cis-Pd}(3)_2\text{Cl}_2$	CD_2Cl_2	29.3, 29.5		22, 109, 110
	CDCl_3	28.5		111
$2\text{-pyr}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)\text{PdMeCN}[\text{BF}_4]_2$	CD_3CN	47.0		75
$\text{cis-PdCl}_2(5)_2$	$\text{CD}_2\text{Cl}_2/203$	34.6		111
$\text{cis-PdBr}_2(5)_2$	$\text{CD}_2\text{Cl}_2/203$	32.1		111
$\text{trans-PdI}_2(5)_2$	$\text{CD}_2\text{Cl}_2/203$	7.0		111
$\text{cis-PdCl}_2(4)_2$	CD_2Cl_2	30.9		111
	CDCl_3	29.4		69
$\text{trans-PdCl}_2(4)_2$	CD_2Cl_2	17.7		111
	$\text{CDCl}_3/203$	17.7		69
$\text{cis-PdBr}_2(4)_2$	$\text{CD}_2\text{Cl}_2/203$	27.9		111
$\text{trans-PdI}_2(4)_2$	$\text{CD}_2\text{Cl}_2/203$	8.9		111
$\text{cis-PdBr}_2(3)_2$	$\text{CD}_2\text{Cl}_2/203$	20.5		111
$\text{trans-PdI}_2(3)_2$	$\text{CD}_2\text{Cl}_2/203$	9.6		111
$\text{PdCl}_2(5)_2$	CD_2Cl_2	6.3		111
$\text{PdBr}_2(5)_2$	CD_2Cl_2	4.35		111
$\text{PdI}_2(5)_2$	CD_2Cl_2	0.55		111
$\text{Pd}_2\text{Cl}_2(4)_2$	CDCl_3	5.2		111
$\text{Pd}_2\text{Br}_2(4)_2$	CDCl_3	3.28		111
$\text{Pd}_2\text{I}_2(4)_2$	CDCl_3	-0.16		111
$\text{Pd}_2\text{Cl}_2(3)_2$	CD_2Cl_2	4.4		22
	CDCl_3	4.4		111
$\text{Pd}_2\text{Br}_2(3)_2$	CDCl_3	2.92		111
$\text{Pd}_2\text{I}_2(3)_2$	CD_2Cl_2	-0.44		111
$\text{Pd}_2\text{Cl}_2(5)_2(\mu\text{-DMAD})$	CDCl_3	34.1		111
$\text{Pd}_2\text{Cl}_2(4)_2(\mu\text{-DMAD})$	CDCl_3	35.5, 35.3, 33.8, 33.3		111
$\text{Pd}_2\text{Cl}_2(3)_2(\mu\text{-DMAD})$	CDCl_3	35.8		111
$\text{Pd}_2(\text{H}_2\text{O})_2(5)_2[\text{BF}_4]$	CD_3CN	-21.8		111
	D_2O	-19.8		111
$\text{Pd}_2(\text{H}_2\text{O})_2(5)_2[\text{PF}_6]$	CD_3CN	-22.2		111
$\text{Pd}_2(\text{H}_2\text{O})_2(5)_2[\text{B}(\text{C}_6\text{H}_5)_4]_2$	CD_3COCD_3	-22.6		111
$\text{Pd}(3)_2\text{Cl}[\text{PF}_6]$	CDCl_3	42.7, -42.3		110
$\text{PdMo}(\mu\text{-}3)_2(\mu\text{-CO})(\text{CO})_2\text{Cl}_2$	CDCl_3	21.67, 31.09	(9.7)	112
$[\text{t-buNC}]_2\text{Cl}_2\text{Rh}(\mu\text{-}3)\text{Pd}(\mu\text{-Cl})_2$	CDCl_3	10.3, 11.1		107
$\text{RhPd}(\mu\text{-}3)_2(\text{CO})\text{Cl}_3$	CD_2Cl_2	21.9, 16.1	113 (17.4) 2.3 ($^3J_{\text{RhP}}$)	113, 121
$\text{RhPd}(\mu\text{-}3)_2(\text{CO})\text{Br}_3$	CDCl_3	19.6, 14.3	112.0 (17.3)	107
$\text{RhPd}(\mu\text{-}3)_2(\text{MeNC})_2\text{Cl}_2[\text{PF}_6]$	CDCl_3	26.9, 17.5	108.9 (17.7)	107
$\text{RhPd}(\mu\text{-}3)_2(\text{MeNC})_2\text{Cl}_2[\text{B}(\text{C}_6\text{H}_5)_4]$	CDCl_3	7.9	94.2	107
$\text{RhPd}(\mu\text{-}3)_2(\text{MeNC})_2\text{Cl}_2[\text{B}(\text{C}_6\text{H}_5)_4]$	CDCl_3	27.6	109.3 (17.1)	107
$\text{Pd}\{[(\text{C}_6\text{H}_5)_2\text{P}]_2\text{pyr}\}_2\text{Cl}_2$		28.0, -1.6		77
$\{\text{Pd}\{[(\text{C}_6\text{H}_5)_2\text{P}]_2\text{pyr}\}_2\text{Br}_2\}_n$		18.1		77
$\text{HT}^+[\text{Pd}_2\text{Cl}_2(\mu\text{-Me}_2\text{Ppyr})_2]$		-23.56		114
$\text{HT}^+[\text{Pd}_2\text{Br}_2(\mu\text{-Me}_2\text{Ppyr})_2]$		-25.83		114
$\text{HT}^+[\text{Pd}_2\text{I}_2(\mu\text{-Me}_2\text{Ppyr})_2]$		-30.17		114
$\text{HH}^+[\text{Pd}_2\text{Cl}_2(\mu\text{-Me}_2\text{Ppyr})_2]^a$		-33.17		114
$\text{HH}^+[\text{Pd}_2\text{Br}_2(\mu\text{-Me}_2\text{Ppyr})_2]^a$		-36.29		114
$\text{HH}^+[\text{Pd}_2\text{I}_2(\mu\text{-Me}_2\text{Ppyr})_2]^a$		-41.73		114
$\text{HT}^+[\text{PdPtCl}_2(\mu\text{-Me}_2\text{Ppyr})_2]$		-20.98	3910 ($^1J_{\text{PPt}}$)	114
$\text{HT}^+[\text{PdPtBr}_2(\mu\text{-Me}_2\text{Ppyr})_2]$		-22.88	3849 ($^1J_{\text{PPt}}$)	114
$\text{HT}^+[\text{PdPtI}_2(\mu\text{-Me}_2\text{Ppyr})_2]$		-26.79	3764 ($^1J_{\text{PPt}}$)	114
$\text{HT}^+[\text{Pd}_2\text{Cl}_2(\mu\text{-}3)_2]$		-3.72		114
$\text{HT}^+[\text{Pd}_2\text{Br}_2(\mu\text{-}3)_2]$		2.31		114
$\text{HT}^+[\text{Pd}_2\text{I}_2(\mu\text{-}3)_2]$		0.37		114
$\text{HH}^+[\text{Pd}_2\text{Cl}_2(\mu\text{-}3)_2]^a$		-12.38		114
$\text{HH}^+[\text{Pd}_2\text{Br}_2(\mu\text{-}3)_2]^a$		-14.31		114
$\text{HH}^+[\text{Pd}_2\text{I}_2(\mu\text{-}3)_2]^a$		-16.6		114
$\text{HT}^+[\text{PdPtCl}_2(\mu\text{-}3)_2]$		7.06, -7.52	4049 ($^1J_{\text{PPt}}$)	114
	CDCl_3	7.4, -6.7	4048 ($^1J_{\text{PPt}}$)	117
$\text{HT}^+[\text{PdPtBr}_2(\mu\text{-}3)_2]$		5.89, -8.89	3978 ($^1J_{\text{PPt}}$)	114
$\text{HH}^+[\text{PdPtI}_2(\mu\text{-}3)_2]$	CDCl_3	-0.06	3213 ($^1J_{\text{PPt}}$)	117
$\text{HT}^+[\text{PdPtI}_2(\mu\text{-}3)_2]$		3.46, -10.93	3894 ($^1J_{\text{PPt}}$)	114
	CDCl_3	3.9, -10.5	3891 ($^1J_{\text{PPt}}$)	117
$\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(t\text{-BuNC})\text{Pd}(\mu\text{-}3)(t\text{-BuNC})\text{Cl}[\text{PF}_6]$	CDCl_3	37.19	148.4 ($^1J_{\text{PRh}}$)	115
$\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(t\text{-BuNC})\text{Pd}(\mu\text{-}3)(t\text{-BuNC})\text{Cl}[\text{Cl}]$	CDCl_3	37.19	148.4 ($^1J_{\text{PRh}}$)	115
$(\eta\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})(\mu\text{-}3)\text{PdCl}_2$	CDCl_3	38.92	158.7 ($^1J_{\text{PRh}}$)	115
$\text{PdRu}(3)_2(\text{CO})_2\text{Cl}_2$	CD_2Cl_2	38.9, 17.9		22
$\text{PdRu}(3)_2(\text{CO})_2\text{Cl}_2$	CD_2Cl_2	20.1, 16.5		22
$\text{Mo}_2[2\text{-(C}_6\text{H}_5)_2\text{Ppyr}(6\text{-O}^-)]\text{-PdCl}_2$	CDCl_3	16		116
$\text{Mo}_2[2\text{-(C}_6\text{H}_5)_2\text{Ppyr}(6\text{-O}^-)]\text{-PdBr}_2$	CDCl_3	16		116
$\text{PdCl}_2[2\text{-(C}_6\text{H}_5)_2\text{Ppyr}(6\text{-O}^-)]_2$	CDCl_3	17		116
$[\text{PdCl}(\text{NIPHOSH-OH})(\text{PMe}_3)][\text{PdCl}_3(\text{PMe}_3)]^b$	CD_3CN	75.5		79
$[\text{PdCl}(\text{NIPHOSH-OMe})(\text{PMe}_3)][\text{SbF}_6]^b$	CD_3CN	107.7		79
$[\text{PdCl}(\text{NIPHOS})(\text{PMe}_3)]\text{PdCl}_3(\text{PMe}_3)]^b$	CDCl_3	169		79

^a These complexes are only observed spectroscopically. ^b NIPHOS (38) = 2-(2-pyridyl)-4,5-dimethylphosphorin.

Table 4. ^{31}P NMR for Platinum Pyridylphosphine Complexes

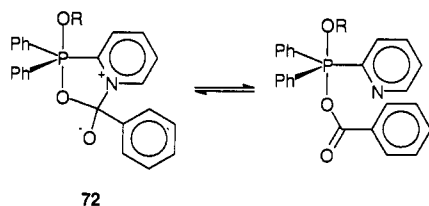
platinum complexes	solvent/temp (K)	δ (ppm)	1J (Pt-P) [$^2J_{\text{PP}}$]	ref(s)
Pt(5) ₄	CDCl ₃ /228	30.1	3829	76
		-538.3 [δ Pt]	3840	
Pt(3) ₃	toluene- <i>d</i> ₈	57.02	4444	76
	228	-300.3 [δ Pt]	4433	
<i>trans</i> -Pt(H)Cl(3) ₂	CD ₂ Cl ₂ /298	30.00	3031	76
<i>trans</i> -PtIme(3) ₂	CDCl ₃ /298	26.82	3078	76
<i>trans</i> -PtIme(5) ₂	CDCl ₃ /298	25.64	3133	76
<i>cis</i> -PtMe ₂ (3) ₂	CDCl ₃	27.3	1875	71
<i>trans</i> -PtMeCl(3) ₂	CDCl ₃	22.0	3157	71
<i>trans</i> -PtMeI(3) ₂	CDCl ₃	25.9	3091 [12]	71
PtMe(η^2 -3)(3)[B(C ₆ H ₅) ₄]	CDCl ₃	-17.6	1391 [12]	71
		19.2	4226 [12]	
<i>trans</i> -PtMe(SnCl ₃)(3) ₂		61.7	3060	71
			217 ($^2J_{\text{SnP}}$)	
<i>cis</i> -Pt(3) ₂ I ₂	CDCl ₃	6.7	3514	70, 117
		11.9	3453	118
<i>trans</i> -Pt(3) ₂ I ₂	CDCl ₃	9.8	2503	70, 117, 118
[Pt(3) ₂ I]I	CDCl ₃	19.3	3637	117, 118
		-61.2	3241	
Pt(3) ₂ (η^2 -CH ₂ =CHCN)	CDCl ₃ /298	30.7	3445 [34.7]	76
		31.7	3969	
Pt(5) ₂ (η^2 -CH ₂ =CHCN)	CDCl ₃ /228	34.6	3406 [31.9]	76
		35.4	3934	
Pt(3) ₂ (η^2 -CH ₂ =CMeCN)	CDCl ₃ /298	31.3	3538 [35.2]	76
		31.3	3718	
Pt(3) ₂ (η^2 -CHMe=CHCN)	CDCl ₃ /298	31.8	3265 [38.5]	76
		32.6	4095	
Pt(3) ₂ (η^2 -CHMe=CHCN)	CDCl ₃ /298	31.6	3240 [39.4]	76
		32.1	4086	
Pt(3) ₂ (η^2 -C ₄ H ₂ O ₃)	CDCl ₃ /298	27.0	3841	76
Pt(3) ₂ [η^2 - <i>cis</i> -(CHCO ₂ Et) ₂]	CDCl ₃ /298	30.0	3750	76
Pt(3) ₂ [η^2 - <i>trans</i> -(CHCO ₂ Et) ₂]	CDCl ₃ /298	28.1	3815	76
{Pt}[(C ₆ H ₅) ₂ P] ₂ pyr] ₂ Cl ₂] _n		14.3	3647	77
<i>trans,trans</i> -Pt ₂ {[μ -(C ₆ H ₅) ₂ P] ₂ pyr] ₂ I ₄ }		6.2	2595	77
<i>HT</i> -[Pt ₂ Cl ₂ (μ -Me ₂ Ppyr) ₂]		-31.78	3985 [18.9]	114
			213 ($^2J_{\text{PPt}}$)	
<i>HT</i> -[Pt ₂ Br ₂ (μ -Me ₂ Ppyr) ₂]		-34.13	3919 [18.9]	114
			212.4 ($^2J_{\text{PPt}}$)	
<i>HT</i> -[Pt ₂ I ₂ (μ -Me ₂ Ppyr) ₂]		-38.00	3827 [18.9]	114
			199.1 ($^2J_{\text{PPt}}$)	
<i>HH</i> -[Pt ₂ I ₂ (μ -Me ₂ Ppyr) ₂] ^a		-16.84	2957	114
			131.2 ($^2J_{\text{PPt}}$)	
<i>HT</i> -[PtPdI ₂ (μ -Me ₂ Ppyr) ₂]		-37.16	3910 [14.5]	114
			90.1 ($^2J_{\text{PPt}}$)	
<i>HT</i> -[PtPdBr ₂ (μ -Me ₂ Ppyr) ₂]		-39.34	3849 [15.6]	114
			71.2 ($^2J_{\text{PPt}}$)	
<i>HT</i> -[PtPdI ₂ (μ -Me ₂ Ppyr) ₂]		-42.96	3764 [16.7]	114
			37.8 ($^2J_{\text{PPt}}$)	
<i>HH</i> -[PtPdI ₂ (μ -Me ₂ Ppyr) ₂] ^a		-27.08	2912	114
<i>HT</i> -[Pt ₂ Cl ₂ (μ -3) ₂]		-2.29	4128 [17.8]	114
	CDCl ₃	-1.5	4124 [17.8]	117
<i>HT</i> -[Pt ₂ Br ₂ (μ -3) ₂]		-3.75	4048 [17.8]	114
			213.5 ($^2J_{\text{PPt}}$)	
<i>HT</i> -[Pt ₂ I ₂ (μ -3) ₂]		-6.25	3965 [20.0]	114
	CDCl ₃	-5.7	3905 [17.7]	117
<i>HH</i> -[Pt ₂ Cl ₂ (μ -3) ₂]		14.64		114
	CDCl ₃	9.6	3263	117
<i>HH</i> -[Pt ₂ Br ₂ (μ -3) ₂]		12.17	3589	114
			160.1 ($^2J_{\text{PPt}}$)	
<i>HH</i> -[Pt ₂ I ₂ (μ -3) ₂]		9.34	3263	114
	CDCl ₃	9.6	3263	117
<i>HT</i> -[PtPdCl ₂ (μ -3) ₂]		-7.52	4049 [14.5]	114
	CDCl ₃	-6.7	4048 [14.3]	117
<i>HT</i> -[PtPdBr ₂ (μ -3) ₂]		-8.89	3978 [15.6]	114
			91.2 ($^2J_{\text{PPt}}$)	
<i>HH</i> -[PtPdI ₂ (μ -3) ₂]	CDCl ₃	-0.06	3213	117
<i>HT</i> -[PtPdI ₂ (μ -3) ₂]		-10.93	3894 [16.1]	114
	CDCl ₃	-10.5	3891 [16.0]	117
<i>cis</i> -Pt(3) ₂ Cl ₂	CD ₂ Cl ₂	11.62	3675.6	113
	CDCl ₃	11.6	3676	117, 118
[Pt(3) ₂ Cl]Cl	CDCl ₃	15.2	3304	117, 118
		-50.03	3339	
Pt(3) ₂ Br ₂	CD ₂ Cl ₂	10.86	3618	113
Pt(3-PO)Br ₄		25.4		82
PtCl ₂ [pyr(CH ₂) ₂ PH(C ₆ H ₅)]		33.64		74

Table 4 (Continued)

platinum complexes	solvent/temp (K)	δ (ppm)	1J (Pt-P) [$^2J_{PP}$]	ref(s)
PtMo(μ -3) ₂ (μ -CO)(CO) ₂ Cl ₂	CDCl ₃	34.4	3064	119
PtRh(3) ₂ (CO)Cl ₃	CD ₂ Cl ₂	1.04	4035 [14.0] ≈ 133 ($^2J_{PPt}$)	113
PtRh(3) ₂ (CO)Cl ₅	CD ₂ Cl ₂	-17.9	2793.3 [19.7] 63.0 ($^2J_{PPt}$)	113
PtRh(3) ₂ (CO)Br ₃	CD ₂ Cl ₂	0.13	3950 [15]	113
PtRh(3) ₂ (CO)Br ₅	CD ₂ Cl ₂	-20.7	2776 [15] 368 ($^2J_{PPt}$)	113
[Pt(3) ₂ Cl][Rh(CO) ₂ Cl ₂]	CD ₂ Cl ₂	15.24	3704	113
(η -C ₅ H ₅)Rh(μ -CO)(μ -3)Pt(Me) ₂	CDCl ₃	50.0	125.6 ($^2J_{PPt}$)	115
(η -C ₅ H ₅)Rh(Cl)(μ -3)Pt(CO)Cl	CDCl ₃	40.93	165.9 ($^2J_{PPt}$)	115
[Pt(3) ₂ Cl][Rh(CO) ₂ Cl ₂]	CDCl ₃	15.2, -50.3	3704, 3339	117
[Pt(3) ₂ I][PF ₆]	CDCl ₃	19.3, -61.2	3637, 3241	117
PtRh[P(C ₆ H ₅) ₂](pyrCH[P(C ₆ H ₅) ₂]) ₂ - (pyrCH ₂ P(C ₆ H ₅) ₂)(P(C ₆ H ₅) ₃)[BF ₄] ₂	CH ₂ Cl ₂ /163	157.2 29.4 27.62 19.62 17.55	129 (J_{RhP}) 130 3115 (J_{PtP})	120
[PtCl(NIPHOS)P(C ₆ H ₅) ₃][PtCl ₃ P(C ₆ H ₅) ₃] ^b	CDCl ₃	155.1	4526	79
[PtCl(NIPHOS)(PMeC ₆ H ₅) ₂][PtCl ₃ (PMeC ₆ H ₅) ₂] ^b	CDCl ₃	155.0	4582	79
[PtCl(NIPHOS)(PMe ₂ C ₆ H ₅)][PtCl ₃ (PMe ₂ C ₆ H ₅)] ^b	CDCl ₃	154.8	4634	79
[PtCl(NIPHOS)(PMe ₃)][PtCl ₃ (PMe ₃)] ^b	CDCl ₃	152.0	4658	79
[PtCl(NIPHOS)(Pbu ₃)][PtCl ₃ (Pbu ₃)] ^b	CDCl ₃	151.6	4536	79
[PtCl(NIPHOSH.OH)(P(C ₆ H ₅) ₃)] ^{+ b}	CDCl ₃	50.9	3936	79
[PtCl(NIPHOSH.OH)(PMe(C ₆ H ₅) ₂)] ^{+ b}	CDCl ₃	53.5	3987	79
[PtCl(NIPHOSH.OH)(PMe ₂ C ₆ H ₅)] ^{+ b}	CDCl ₃	52.8	4002	79
[PtCl(NIPHOSH.OH)(PMe ₃)] ^{+ b}	CDCl ₃	54.7	4059	79
[PtCl(NIPHOSH.OH)(Pbu ₃)] ^{+ b}	CDCl ₃	54.5	4152	79
[PtCl(NIPHOSH.OH)(AsMe ₂ C ₆ H ₅)] ^{+ b}	CDCl ₃	55.0	3873	79
[PtCl(NIPHOSH.OMe)(PMe ₃)] ^{+ b}	CD ₃ CN	80.0	4156	79
[PtCl(NIPHOSH.Oi-Pr)(PMe ₃)] ^{+ b}	CDCl ₃	72.0	4138	79
[PtCl(NIPHOSH.Oisoamyl)(PMe ₃)] ^{+ b}	CDCl ₃	75.4	4162	79
[PtCl(NIPHOSH.OC ₆ H ₅)(PMe ₃)] ^{+ b}	CDCl ₃	80.4	4296	79
[PtCl(NIPHOSH.SC ₆ H ₅)(PMe ₃)] ^{+ b}	CDCl ₃	28.6	3872	79

^a Mixture of isomers. ^b NIPHOS (38) = 2-(2-pyridyl)-4,5-dimethylphosphorin.

Scheme 27



(1:100 complex to alkene ratio), hex-1-ene was selectively hydroformylated to heptanal.⁸ These authors noted their inability to remove the tripyridylphosphine rhodium complex from the product as well as their inability to prepare the corresponding tris(3- or 4-pyridylphosphines) from the corresponding bromopyridines.

Addition of propyne to Pd(OAc)₂, (6-Me-2-pyr)₂-P(C₆H₅)₃,¹⁷⁰ and *p*-toluenesulfonic acid in *N*-methylpyrrolidine and methanol, followed by treatment with CO (60 bar) afforded (99.9%) methyl methacrylate; the yield was slightly less using 4 (98.3%) or using (2-pyr)-(4-MeC₆H₄)P(C₄H₉) (98.9%).¹⁷¹

Several new pyridylphosphine catalysts FeRh(3)₂(CO)₃Cl, NiRh(3)₂(CO)Cl₃, and CoRh(3)₂(CO)Cl₃ have recently been prepared⁷² from Fe(3)₂(CO)₂(CS₂), Ni(3)₂(CO)₂, and CoRh(3)₂Cl₂, respectively, and successfully used in the carbonylation of methanol. The use of binuclear metal pyridylphosphine complexes in this carbonylation process afforded acetic acid in >94.3% and a combination of acid and methyl ester in >99.11% total yield.

Treatment of cyclopentene with (C₆H₁₁)P[(CH₂)₂(2-pyr)] and Ni(COD)₂ under CO₂ (1 bar) at 20 °C afforded (95%) a bicyclic Ni complex intermediate, which was readily transformed to a series of functionalized cyclopentanecarboxylic acid derivatives.¹³⁶

Tetradec-1-ene was hydroformylated⁷⁸ using a water-soluble catalyst consisting of Rh₄(CO)₁₂ and a surface active sulfobetaine derivative of 5. The best yield (79%) was obtained using 5 sulfalkylated by octane-1,2-sultone, as the ligand.

Gladiali et al.¹⁷² utilized (η -C₅H₅)Rh₂(μ -CO)(μ -3)-(CO)Cl as a hydroformylation catalyst; the formation of the intermediates was followed by ³¹P NMR spectra.

2. Chlorinations

When primary or secondary alkyl alcohols were treated with 2-pyr(CH₂)₂P(C₆H₅)₂ in CCl₄/CHCl₃ at 35–45 °C, high yields of the corresponding alkyl chloride were obtained.⁴⁵ The reaction complexes were studied by ³¹P NMR, and the rate constants were presented.

3. Mitsunobu Esterification

The use of 3 in the Mitsunobu reaction (treatment of carboxylic acids with alcohols in the presence of diisopropyl azodicarboxylate and triphenylphosphine) greatly facilitates the removal of the phosphine oxide byproduct, while maintaining comparable yields of the desired ester.¹⁷⁵ Recycling of the pyridylphosphine was accomplished by the reduction of the corresponding

Table 5. ^{31}P NMR for Rhodium Pyridylphosphine Complexes^a

rhodium complexes	solvent/temp (K)	δ (ppm)	$^1J_{\text{RhP}}$ [$^2J_{\text{PP}}$]	ref(s)
$\text{Rh}(\text{bpy})_2(\text{CO})\text{Cl}$	CDCl_3	30.13	127.8	110, 121
$\text{Rh}(\text{bpy})_2(\text{CO})\text{Br}$	CDCl_3	29.1	125.9	110
$\text{Rh}(\text{MeNC})_2(\text{bpy})_2[\text{PF}_6]$	$\text{CDCl}_3/233$	28.3	130.5	110
$\text{Rh}(\text{MeNC})_2(\text{bpy})_2[\text{B}(\text{C}_6\text{H}_5)_4]$	$\text{CDCl}_3/233$	28.3	128.5	110
$\text{RhPd}(\mu\text{-bpy})_2(\text{CO})\text{Cl}_3$	CD_2Cl_2	21.9, 16.1	112.7 [17.4] 2.3 ($^2J_{\text{RhP}}$)	110, 113, 121
$\text{RhPd}(\mu\text{-bpy})_2(\text{CO})\text{Br}_3$	CDCl_3	19.6, 14.3	112.0 [17.3]	110
$\text{RhPd}(\mu\text{-bpy})_2(\text{MeNC})_2\text{Cl}_2[\text{PF}_6]$	CDCl_3	26.9, 17.5	108.9 [17.7]	110
$\text{RhPd}(\mu\text{-bpy})_2(\text{MeNC})_2\text{Cl}_2[\text{B}(\text{C}_6\text{H}_5)_4]$	CDCl_3	7.9	94.2	110
$\text{RhPd}(\mu\text{-bpy})_2(\text{MeNC})_2\text{Cl}_2[\text{B}(\text{C}_6\text{H}_5)_4]$	CDCl_3	27.6	109.3 [17.1]	110
$\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3](\text{CO})(\text{bpy})\text{Cl}$	toluene- d_8	27.8	128	107
$\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{bpy})(\text{CO})(\text{Cl})$	215	41.0	140.8 [22]	172
		45.8	154.8 [22]	
$\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3](\text{bpy})_2(\text{CO})(\text{Cl})$	215	42.2	154.5 [37.8]	172
		45.9	155.1 [37.8]	
$[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-DMA})(\mu\text{-bpy})\text{Rh}(\text{CO})\mu\text{-Cl}]_2$	$\text{CD}_2\text{Cl}_2/298$ 225	53.4 54.1 55.3	175.9 [4.8] 175.6 [4.8] 174.9 [4.6]	145
$[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-DMA})(\mu\text{-bpy})\text{Rh}(\text{CO})(\text{SO}_2)\text{Cl}]$	CD_2Cl_2	60.9	162 [3.7]	145
$\text{Rh}(\text{C}_6\text{H}_{12})(\text{bpy})\text{Cl}$	CDCl_3	29.7, 30.6	150.2, 150.3	122
	CD_2Cl_2	29.3	150.1	107
$\text{Rh}(\text{acac})(\text{Cl})\text{CH}_2[\text{Ppyr}(\text{C}_6\text{H}_5)]_2\text{CH}_2[\text{Cl}]$		63.7, 90.0 62.9, 93.7	122, 139 [15] 123, 135 [14]	147
$\text{Rh}(\text{acac})(\text{Cl})\text{CH}_2[\text{Ppyr}(\text{C}_6\text{H}_5)]_2(\text{CH}_2)_3[\text{Cl}]$		22.8, 60.9 20.4, 60.2 23.3, 61.0 22.9, 60.7	116, 130 [36] 116, 131 [37] 116, 125 [50] 118, 125 [51]	147
$\text{Rh}(\text{dpm})(\text{Cl})\text{CH}_2[\text{Ppyr}(\text{C}_6\text{H}_5)]_2(\text{CH}_2)_2[\text{Cl}]$		62.9, 88.1 62.4, 91.2	121, 140 [16] 122, 136 [14]	147
$\text{Rh}(\text{dpm})(\text{Cl})\text{CH}_2[\text{Ppyr}(\text{C}_6\text{H}_5)]_2(\text{CH}_2)_3[\text{Cl}]$		20.8, 59.9 19.5, 58.6	116, 131 [38] 115, 131 [38]	147
$\text{Rh}(\text{dpm})(\text{Cl})\text{CH}_2[\text{pyrPMe}_2][\text{Cl}]$		23.8, 54.0	125, 131 [46]	147
$\text{Rh}(\text{acac})(\text{Cl})(\text{CH}_2\text{Cl})[\text{Ppyr}(\text{C}_6\text{H}_5)]_2\text{CH}_2$		-18.8, -11.0 -12.9	118, 124 [84] 117	147
$\text{Rh}(\text{acac})(\text{Cl})(\text{CH}_2\text{Cl})[\text{Ppyr}(\text{C}_6\text{H}_5)]_2(\text{CH}_2)_2$		58.6, 61.8 51.5	137, 147 [17] 137	147
$\text{Rh}(\text{acac})(\text{Cl})(\text{CH}_2\text{Cl})[\text{Ppyr}(\text{C}_6\text{H}_5)]_2(\text{CH}_2)_3$		19.0, 22.2 24.2	126, 134 [40] 127	147
$\text{Rh}(\text{dpm})(\text{Cl})(\text{CH}_2\text{Cl})[\text{Ppyr}(\text{C}_6\text{H}_5)]_2\text{CH}_2$		-17.5, -11.6 -11.7	117, 126 [85] 117	147
$\text{Rh}(\text{dpm})(\text{Cl})(\text{CH}_2\text{Cl})[\text{Ppyr}(\text{C}_6\text{H}_5)]_2(\text{CH}_2)_2$		55.2, 59.2 53.4	136, 148 [19] 137	147
$\text{Rh}(\text{dpm})(\text{Cl})(\text{CH}_2\text{Cl})[\text{Ppyr}(\text{C}_6\text{H}_5)]_2(\text{CH}_2)_3$		18.1, 20.7 24.3	126, 138 [40] 129	147
$\text{Rh}(\text{dpm})[\text{Ppyr}(\text{C}_6\text{H}_5)]_2\text{CH}_2$		-16.2	159	147
$\text{Rh}(\text{dpm})[\text{Ppyr}(\text{C}_6\text{H}_5)]_2(\text{CH}_2)_2$		75.2	189 [48]	147
$\text{Rh}(\text{dpm})[\text{Ppyr}(\text{C}_6\text{H}_5)]_2(\text{CH}_2)_3$		39.9	178 [75]	147
$\text{Rh}(\text{dpm})(\text{pyrPMe}_2)$		27.7	186	147
$\text{Rh}(\text{acac})[\text{Ppyr}(\text{C}_6\text{H}_5)]_2(\text{CH}_2)_2$		73.8	188 [49]	147
$\text{Rh}(\text{acac})[\text{Ppyr}(\text{C}_6\text{H}_5)]_2(\text{CH}_2)_3$		38.9	178 [73]	147
$\text{Rh}_2(\text{form})_2(\mu\text{-O}_2\text{CCF}_3)(\mu\text{-bpy})(\text{O}_2\text{CCF}_3)$	$\text{CDCl}_3/225$ 310	-34.36 30.21 29.53 30.9	82.8 [55.4] 127.0 [5.7] 126.4 [5.3] 127.6 [3.3]	142
$\text{Rh}(\text{form})_2(\mu\text{-bpy})_2(\text{O}_2\text{CCF}_3)_2$	$\text{CD}_3\text{CN}/310$ $\text{CDCl}_3/225$ $\text{CDCl}_3/310$ $\text{CD}_3\text{CN}/310$	-96.05 29.01 25.83 29.68		142
$[\text{Rh}_2(\text{form})_2(\mu\text{-bpy})(\mu\text{-O}_2\text{CCF}_3)][\text{PF}_6]$	$\text{CDCl}_3/310$	26.8	122.2 [5.2]	142
$\text{Rh}_2(\text{form})_2(\mu\text{-bpy})_2[(\text{PF}_6)_2]$	$\text{CDCl}_3/310$	28.74	131.1	142
$\text{Rh}_2(\text{form})_2(\mu\text{-bpy})(\mu\text{-O}_2\text{CCF}_3)[\text{Cl}]$	$\text{CDCl}_3/225$	24.35	164.5 [5.8]	142
$\text{Rh}_2(\text{form})_2(\mu\text{-bpy})(\mu\text{-O}_2\text{CCF}_3)[\text{Br}]$	$\text{CDCl}_3/310$	28.79	122.2 [5.4]	142
$\text{Rh}_2(\text{form})_2(\mu\text{-bpy})_2(\mu\text{-O}_2\text{CCF}_3)[\text{Cl}]$	$\text{CDCl}_3/310$	27.90	131.3	142
$\text{Rh}_2(\text{form})_2(\mu\text{-bpy})_2\text{I}_2$	$\text{DCCl}_3/310$	27.82	129.9	142
$\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{bpy})$	CDCl_3	53.80	199.8	143
$(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-CO})(\mu\text{-bpy})\text{Rh}(\text{CO})\text{Cl}$	CDCl_3	52.10	175.6 [5.3]	143
$(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\mu\text{-bpy})(\mu\text{-SO}_2)\text{Rh}(\text{CO})\text{Cl}$	CDCl_3	60.3	162.2 [3.8]	143
$[(t\text{-buNC})_2\text{Cl}_2\text{Rh}(\mu\text{-bpy})\text{Pd}(\mu\text{-Cl})]_2$	CDCl_3	10.3, 11.1		107
$\text{Rh}(\text{acac})[\text{Ppyr}(\text{C}_6\text{H}_5)]_2\text{CH}_2$		-19.2	164	147
$\text{Rh}(\text{acac})[\text{Ppyr}(\text{C}_6\text{H}_5)]_2(\text{CH}_2)_2$		70.0	194 [51]	147
$\text{Rh}(\text{acac})[\text{Ppyr}(\text{C}_6\text{H}_5)]_2(\text{CH}_2)_3$		37.3	182	147
$\text{Rh}(\text{dpm})[\text{Ppyr}(\text{C}_6\text{H}_5)]_2\text{CH}_2$		-18.5	164	147
$\text{Rh}(\text{dpm})[\text{Ppyr}(\text{C}_6\text{H}_5)]_2(\text{CH}_2)_2$		72.1	194 [52]	147
$\text{Rh}_2\text{Sn}_2(\text{CO})_2\text{Cl}_6[\mu\text{-2,6-pyr}(\text{P}(\text{C}_6\text{H}_5)_2)_2]_2$	$\text{C}_6\text{D}_6/298$	42.2 67.1	91.8 141.0	149

Table 5 (Continued)

rhodium complexes	solvent/temp (K)	δ (ppm)	$^1J_{\text{RhP}}$ [$^2J_{\text{PP}}$]	ref(s)
$\text{Rh}_2(\text{CO})_2\text{Cl}_2[\mu\text{-}2,6\text{-pyr}(\text{P}(\text{C}_6\text{H}_5)_2)_2]_2$	$\text{CDCl}_3/293$	28.6 29.3 30.0	132 124 127	149
$\text{Rh}_4[2,6\text{-pyr}(\text{P}(\text{C}_6\text{H}_5)_2)_2]_2(\mu\text{-CO})(\text{CO})_2(\mu\text{-Cl})_2\text{Cl}_3$		39.9 36.2	129.7 149.7	108, 149
$\text{Rh}_4[\mu\text{-}2,6\text{-pyr}(\text{P}(\text{C}_6\text{H}_5)_2)_2]_2(\mu\text{-SO}_2)(\text{CO})_2\text{Cl}_4$		35.7 30.7	131 138	150
$[\text{Rh}_2(\text{CO})[\mu\text{-}2,6\text{-pyr}(\text{P}(\text{C}_6\text{H}_5)_2)_2]_2(\text{CH}_3\text{OH})\text{Cl}]^+$		31.1 20.4	128.2 128.9	150
<i>rac</i> - $[(\text{C}_6\text{H}_5)_2\text{pyrP}]_2(\text{CH}_3)[\text{Rh}(\text{CO})\text{Cl}_2]_2$	$\text{DMSO-}d_6$	36.9	161 [67]	19
<i>meso</i> - $[(\text{C}_6\text{H}_5)_2\text{pyrP}]_2(\text{CH}_3)_2\text{Rh}_2\text{Cl}_3[\text{Rh}(\text{CO})\text{Cl}_2]_2$	$\text{CD}_3\text{OD-CD}_3\text{CN}$	24.0	≈ 112	19
$[\text{Rh}_2[\mu\text{-}[(\text{C}_6\text{H}_5)_2\text{P}]\text{pyr}](\mu\text{-CO})(\mu\text{-I})][\text{B}(\text{C}_6\text{H}_5)_4]$	$\text{CDCl}_3/298$	61.3 -41.3	153 135	123
$\{(\text{C}_6\text{H}_5)_2\text{Rh}[(\text{C}_6\text{H}_5)_2\text{Ppyr}]_2\}_2$	CD_2Cl_2	25.1	144	73
$\{(\text{CO})_2\text{Rh}[(\text{C}_6\text{H}_5)_2\text{Ppyr}]_2\}_2[\text{BF}_4]$	$\text{CD}_2\text{Cl}_2/183$	40.5	75	73
$\text{RhPt}(\text{C}_6\text{H}_5)_2(\text{CO})\text{Cl}_3$	CD_2Cl_2	24.6	114 [2.9]	113
$\text{RhPt}(\text{C}_6\text{H}_5)_2(\text{CO})\text{Cl}_5$	CD_2Cl_2	27.9	110	113
$\text{RhPt}(\text{C}_6\text{H}_5)_2(\text{CO})\text{Br}_3$	CD_2Cl_2	24.0	110	113
$\text{RhPt}(\text{C}_6\text{H}_5)_2(\text{CO})\text{Br}_5$	CD_2Cl_2	27.6	112	113
$\text{Rh}_2(\text{C}_6\text{H}_5)_2(\mu\text{-CO})\text{Cl}_2$	CD_2Cl_2	44.18	144.0 [16.0] 12.0 (J_{RhRh}) -7.39 ($^2J_{\text{RhP}}$)	121, 124
$(\eta^5\text{-C}_6\text{H}_5)(t\text{-buNC})\text{Rh}(\mu\text{-}3)\text{Pd}(t\text{-buNC})(\text{Cl})[\text{PF}_6]$	CDCl_3	37.19	148.4	115
$(\eta^5\text{-C}_6\text{H}_5)(t\text{-buNC})\text{Rh}(\mu\text{-}3)\text{Pd}(t\text{-buNC})(\text{Cl})[\text{Cl}]$	CDCl_3	37.19	148.4	115
$(\eta^5\text{-C}_6\text{H}_5)(\text{CO})\text{Rh}(\mu\text{-}3)\text{PdCl}_2$	CDCl_3	38.92	158.7	115
$(\eta^5\text{-C}_6\text{H}_5)(\mu\text{-CO})\text{Rh}(\mu\text{-}3)\text{PtMe}_2$	CDCl_3	50.0	190.2 125.6 ($^2J_{\text{PPt}}$)	115
$(\eta^5\text{-C}_6\text{H}_5)(\text{Cl})\text{Rh}(\mu\text{-}3)\text{Pt}(\text{CO})\text{Cl}$	CDCl_3	40.93	152.48 165.9 ($^2J_{\text{PPt}}$)	115
$\text{Rh}_2(\mu\text{-}3)_2(\mu\text{-Cl})(\text{CO})\text{Cl}_3$	248	29.7 23.2	117.2 109.9	125
$\text{Rh}_2(\mu\text{-}3)_2(\text{CO})\text{Cl}_4$	$(\text{ClCH}_2)_2/348$	27.6	≈ 124.5	125
$\text{Rh}_2(\mu\text{-}3)_2(\text{CO})_2\text{Cl}_4$		22.4	109.9	125
$\text{Rh}_2(\mu\text{-}3)_2(t\text{-buNC})_2\text{Cl}_4$		25.3	113.0	125
$\text{Rh}_2(\text{C}_6\text{H}_5)_2(\mu\text{-SO}_2)\text{Cl}_2$		41.70	138.4 [18] -6.2 ($^2J_{\text{PRh}}$)	124
$\text{Rh}_2(\text{CO})[\mu\text{-pyrCH}(\text{P}(\text{C}_6\text{H}_5)_2)_2]_2[\text{B}(\text{C}_6\text{H}_5)_4]_2$	acetone, 293	61.5 37.7	136, 130 (J_d) 30.5, 30.5 (J_d)	126
$\text{PtRh}[\text{P}(\text{C}_6\text{H}_5)_2](\text{pyrCH}[\text{P}(\text{C}_6\text{H}_5)_2]_2)(\text{pyrCH}_2\text{-P}(\text{C}_6\text{H}_5)_2)(\text{P}(\text{C}_6\text{H}_5)_3)[\text{BF}_4]_2$	$\text{CH}_2\text{Cl}_2/163$	157.2	5129 (J_{RhP})	127
		29.4 27.62 19.62 17.5	130 3115 (J_{PP})	
$\text{Rh}[\text{pyrCH}(\text{P}(\text{C}_6\text{H}_5)_2)_2][\text{BF}_4]$	CH_2Cl_2	1.06	115.6 (J_{RhP})	128
$\text{RhAg}[\text{pyrCH}(\text{P}(\text{C}_6\text{H}_5)_2)_2][\text{BF}_4][\text{NO}_3]$	CH_2Cl_2	53.84 25.66	143 (J_{RhP}) [50,37] 543, 468 (J_{AgP}) [50,37]	127
$\text{RhAg}[\text{pyrCH}(\text{P}(\text{C}_6\text{H}_5)_2)_2](\text{CO})_2[\text{BF}_4\text{NO}_3]$	CH_2Cl_2	51.99 49.93	140	127
$\text{RhAu}[\text{pyrCH}(\text{P}(\text{C}_6\text{H}_5)_2)_2\text{Cl}][\text{BF}_4]$	CH_2Cl_2	68.89 42.82	171	127
$\text{RhAu}[\text{pyrCH}(\text{P}(\text{C}_6\text{H}_5)_2)_2\text{Br}][\text{BF}_4]$	CH_2Cl_2	68.34 43.33	170	127
$\text{RhAu}[\text{pyrCH}(\text{P}(\text{C}_6\text{H}_5)_2)_2][\text{BF}_4\text{NO}_3]$	CH_2Cl_2	76.02	~ 162	128
$\{\text{Rh}_2[\text{pyrCH}(\text{P}(\text{C}_6\text{H}_5)_2)_2](\text{CO})_2\}_2[\text{PF}_6]\cdot\text{C}_3\text{H}_6\text{O}$	MeCOMe	62.0	117.9 (J_{RhP}); 293.5, 54.1 (J_{PP}) 134.5 (J_{RhP}); 293.0, 54.0 (J_{PP})	129
$\text{Rh}(\text{CO})(\text{Cl})[\text{pyrCH}(\text{P}(\text{C}_6\text{H}_5)_2)_2]$	MeCOMe	69.1 0.35	168 (J_{RhP}) [107] [108]	129
$\text{Rh}(\mu\text{-S})(\text{CO})_2[\text{pyrCH}(\text{P}(\text{C}_6\text{H}_5)_2)_2]$	CDCl_3	34.1	139	129
$\text{Rh}(\text{CO})\text{ZnCl}(\mu\text{-Cl})\{2,6\text{-pyr}[\text{CH}_2\text{O}(\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2]_2\}(\text{CF}_3\text{SO}_3)$	CH_2Cl_2	26.4	119	46
$[\text{Rh}_2(\text{NBD})_2(\text{NIPHOS})_2][\text{SbF}_6]_2$	CD_3CN	154.9	92.5	130

^a NIPHOS (38) = 2-(2-pyridyl)-4,5-dimethylphosphorin. NBD = norbornadiene. DMA = dimethyl acetylenedicarboxylate. COD = cyclooctadiene. Dpm = 2,2,6,6-tetramethylheptanedioate. acac = acetylacetonate. Form = di-*p*-tolylformamidinate.

P-oxide by a previously reported $\text{CeCl}_3/\text{LiAlH}_4$ procedure.¹⁷³ The mechanism of this esterification has been further studied¹⁷⁴ using ^{31}P NMR, revealing the presence of a dialkoxyphosphorane intermediate in equilibrium with the alkoxyphosphonium carboxylate species; details were presented.

Camp and Jenkins¹⁷⁴ have used **3** in the Mitsunobu reaction to circumvent the difficulties associated with the use of triphenylphosphine oxide.¹⁷⁵ They suggested¹⁷⁴ that **3** stabilizes the (acyloxy)alkoxyphosphorane intermediate through *N*-coordination with the acetoxy carbonyl carbon, thus stabilizing the phosphorane

Table 6. ^{31}P NMR for Molybdenum Pyridylphosphine Complexes

molybdenum complexes	solvent	δ (ppm)	$^1J_{\text{PH}}$	ref
<i>cis</i> -Mo(CO)(3) ₂	CDCl ₃	40.65		112
PdMo(μ -3) ₂ (μ -CO)(CO) ₂ Cl	CDCl ₃	21.67, 31.09	9.7 (3J)	112
2-pyrPH ₂ Mo(CO) ₅	CD ₂ Cl ₂	-83.1	339	29
(2-pyrPH ₂) ₂ Mo(CO) ₄	CD ₂ Cl ₂	-56.0	330	29
32	CDCl ₃	61.1		54
35	CDCl ₃	60.24		54
2-pyr(CH ₂) ₂ PH ₂ Mo(CO) ₄	C ₆ D ₆	-81.8	322	36
2-pyrCH ₂ PH ₂ Mo(CO) ₄	CD ₂ Cl ₂	-1.4	345	36
2-pyr(CH ₂) ₂ PH(C ₆ H ₅)Mo(CO) ₄	CD ₂ Cl ₂	-5.3	337	36
[2-pyr(CH ₂) ₂ PH ₂] ₂ Mo(CO) ₄	THF	-75.7	318	36
2-pyr(CH ₂) ₂ PH ₂ Mo(CO) ₄ P(C ₆ H ₅)H ₂	CD ₂ Cl ₂	-61.8, -74.7	22 ($^2J_{\text{PP}}$)	36
2-pyr(CH ₂) ₂ PH ₂ Mo(CO) ₅	C ₆ D ₆	-80.8	318	36
2-pyrCH ₂ PH(C ₆ H ₅)Mo(CO) ₅	CD ₂ Cl ₂	-4.4	339	36
2-pyr(CH ₂) ₂ PH ₂ [Mo(CO) ₂ (η^5 -C ₅ H ₅)] ₂	CD ₂ Cl ₂	-14.3	334	36
2-pyr(CH ₂) ₂ PH(C ₆ H ₅)[Mo(CO) ₂ (η^5 -C ₅ H ₅)] ₂	CD ₂ Cl ₂	48.8	345	36
2,6-[(C ₆ H ₅) ₂ P]pyr[Mo(CO) ₅] ₂		39.5		25
2,6-[(C ₆ H ₅) ₂ P]pyr[Mo(CO) ₄ pip] ^a		36.5, -4.8	239 ($^1J_{\text{PW}}$)	25
2,6-[(C ₆ H ₅) ₂ P]pyr[Mo(CO) ₄ pip] ₂ ^a			45.6	25
Mo(CO) ₅ (3)	CDCl ₃	40.78		131
Mo(CO) ₄ (3) ₂	CDCl ₃	40.52		131
		40.7		119
Mo ₂ (η -C ₅ H ₅) ₂ (CO) ₄ (3) ₂	CDCl ₃	58.0		132
Mo ₂ [2-(C ₆ H ₅) ₂ Ppyr(6-O)] ₄	CDCl ₃	-8.3		116
Mo ₂ [2-(C ₆ H ₅) ₂ Ppyr(6-O)] ₄ Mo(CO) ₃	CDCl ₃	35		116
Mo ₂ [2-(C ₆ H ₅) ₂ Ppyr(6-O)] ₄ ·PdCl ₂	CDCl ₃	16		116
Mo ₂ [2-(C ₆ H ₅) ₂ Ppyr(6-O)] ₄ ·PdBr ₂	CDCl ₃	16		116
MoPt(μ -3) ₂ (μ -CO)(CO) ₂ Cl ₂	CDCl ₃	34.4	3064 (J_{PP})	119

^a Pip = piperidine.

structure 72 and rendering the carboxylate a much poorer leaving group (Scheme 27). ^{31}P NMR chemical shift data for diverse dialkoxydiphenyl(2-pyridyl)-phosphoranes have been determined¹⁷⁵ and compared to the corresponding triphenylphosphine betaines.

4. Epoxidation of Alkenes

It has been reported¹⁷⁶ that ruthenium(II) complexes, specifically RuCl[(C₆H₅)₂P(CH₂)₂(2-pyr)]₂[ClO₄], promote the oxidation of several alkenes by C₆H₅IO, hypochlorates, and hydrogen peroxide. Typically, the reaction of alkene (0.1 M), catalyst (2 mM), and C₆H₅IO in CH₂Cl₂ at 22 °C afforded average (25–55%) yields of the epoxide.

5. Metal-Catalyzed Cycloadditions

Recently, the Ni(0) *P*-complex catalyzed, one-step, α -pyrone synthesis from CO₂ and diynes has been reported.^{56,57} The use of (2-pyr)(CH₂)₂P(bu)₂ has been shown to give enhanced yields of the desired α -pyrone product(s) over simple trialkylphosphines, suggesting that functionalized phosphines are unique due to intramolecular coordination of the pyridyl moiety to the nickel atom via a six-membered chelate ring. This procedure provides a facile, general, and convenient method for forming α -pyrones.

6. Dimerization of Isoprene

Hoberg and Minato¹⁷⁷ reported the easy Pd-catalyzed dimerization of isoprene, using Pd(acac)₂, (C₆H₁₁)₂P[(CH₂)₂(2-pyr)]₂, and DBU under CO₂ pressure in the presence of tri-*n*-butyltin ethoxide. A mixture of two "C₁₀H₁₆CO₂CH₃" esters was isolated (68%); each major component was characterized. Although these authors noted the "obscure" effect of DBU, no mention was

made to the rationale for the particular pyridylphosphine. A similar functionalization was reported¹³⁵ using cyclooctene.

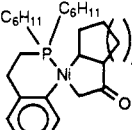
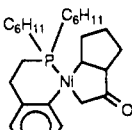
IV. Conclusions

Although pyridylphosphines have been known for nearly five decades, the synthetic and instrumental tools are now available to permit the construction and characterization of new types of complexes and organometallic structures possessing a pyridylphosphine subunit. Synthetic approaches presented in this review can be applied to numerous new combinations as well as applied to the incorporation of other *N*-heterocycles related to pyridine. The use of nitrogen in cryptand construction is quite common; however, the use of phosphorus has been limited, thus expansion of Holm's clathrochelate structures¹⁰ in view of Vögtle's superstructures¹⁷⁸ has great potential.

The metallomacrocycles, derived from pyridylphosphines, are readily prepared and can complex diverse substrates. The preparation of other metallomacrocycles with different structural composition will afford information into unique geometries and the effect on substrate inclusion and/or interactions. The expansion to oligomeric pyridylphosphines will afford access to linear coordination of metal ions, whereas the construction of bridged pyridylphosphine superstructures will lead to polymetallopolymacrocycles.

The catalytic aspects of pyridylphosphines has only recently been explored. The advantage of the basic pyridine coupled with the desirable coordination of phosphine(s) to metal ions offers a utilitarian slant. Application of this feature to reactions currently using triphenylphosphine can simplify the difficult removal of triphenylphosphine oxide, as demonstrated by Camp and Jenkins¹⁷⁴ in their studies of the Mitsunobu reaction.

Table 7. ^{31}P NMR for Other Pyridylphosphine Complexes

complexes	solvent/temp (K)	δ (ppm)	$^1J_{\text{PH}}$	ref(s)
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}_2(\text{CH}_3)_2\text{Co}(\text{C}_6\text{H}_5)_2\text{I}_2$	CDCl_3	35.8		133
$2\text{-pyrPH}_2\text{Ni}(\text{CO})_3$	CD_2Cl_2	-71.1	313	29
$\text{Re}_2(\text{CO})_8[\eta^2, \eta^2\text{-pyrCH}(\text{P}(\text{C}_6\text{H}_5)_2)_2]$	CD_2Cl_2	21.3		148
$\text{Re}_2(\text{CO})_7[\mu\text{-}\eta^1, \eta^4\text{-pyrCH}(\text{P}(\text{C}_6\text{H}_5)_2)_2]$	$\text{CDCl}_3/253$	70.3	24 (J_{PP})	148
$\text{Re}_2\text{Cl}_4(\text{C}_6\text{H}_5)_3$		-12.8	22 (J_{PP})	
$\text{Re}_2\text{Cl}_3(\text{C}_6\text{H}_5)_2[(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_4)\text{Ppyr}]$	$\text{CDCl}_3\text{-CH}_2\text{Cl}_2$ (1:1)	-6.150, -5.45, -0.37	11.1 ($^2J_{\text{PP}}$), 6.7, 4.9 ($^3J_{\text{PP}}$)	23
$\text{Re}_2\text{Cl}_2(\text{C}_6\text{H}_5)_3[\text{PF}_6]$	$\text{CDCl}_3\text{-CH}_2\text{Cl}_2$ (1:1)	-25.81, -0.88, 14.66	16.3 ($^2J_{\text{PP}}$), 9.3, 6.9 ($^3J_{\text{PP}}$)	23, 134
$\text{Re}_2\text{Cl}_2(\text{C}_6\text{H}_5)_3[\text{PF}_6]$	$\text{CDCl}_3\text{-CH}_2\text{Cl}_2$ (1:1)	11.76		23
$\text{Re}_2\text{Cl}_4(\text{C}_6\text{H}_5)_3(\text{PEt}_3)$	$\text{CDCl}_3\text{-CH}_2\text{Cl}_2$ (1:1)	-25.48, -7.24, 13.68		23
$\text{ReCl}_4(\text{C}_6\text{H}_5)_3(\text{Pbu}_3)$	$\text{CDCl}_3\text{-CH}_2\text{Cl}_2$ (1:1)	-29.71, -8.31, 13.73	10.0 ($^2J_{\text{PP}}$), 7.0, 3.9 ($^3J_{\text{PP}}$)	23
$2\text{-pyrPH}_2\text{W}(\text{CO})_5$	CD_2Cl_2	-89.9	343	29
	DMF-d_7	36.1		135
	CD_2Cl_2	38.3		136
$\text{Ru}_3(\mu\text{-}\eta^2\text{C}(\text{O})\text{C}_6\text{H}_5)(\mu_3\text{-}\eta^2\text{-Ppyr}(\text{C}_6\text{H}_5)(\text{CO})_9$	CDCl_3	48.93		146
$\text{Ru}_3(\mu\text{-}\eta^2\text{C}(\text{O})\text{C}_6\text{H}_5)(\mu_3\text{-}\eta^2\text{-Ppyr}(\text{C}_6\text{H}_5)(\text{CO})_9$	CDCl_3	49.53, 26.26	17.60 (J_{PP})	146
$\text{Ru}_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-Ppyr}(\text{C}_6\text{H}_5)(\text{CO})_9$	CDCl_3	118.05		146
$2,6\text{-}[(\text{C}_6\text{H}_5)_2\text{P}]_2\text{pyr}[\text{Cr}(\text{CO})_5]_2$		57.5		25
$2,6\text{-}[(\text{C}_6\text{H}_5)_2\text{P}(\text{O})]_2\text{pyr}[\text{P}(\text{C}_6\text{H}_5)_2\text{Cr}(\text{CO})_5]$		58.3, 19.3	2.4 (J_{PP})	25
$2,6\text{-}[(\text{C}_6\text{H}_5)_2\text{P}]_2\text{pyr}[\text{W}(\text{CO})_5]_2$		23.1	239 ($^1J_{\text{PW}}$)	25
$2,6\text{-}[(\text{C}_6\text{H}_5)_2\text{P}]_2\text{pyr}[\text{W}(\text{CO})_5]$		21.7, -3.3		25
$\text{Cu}_2(\mu\text{-}3)_2(\text{MeCN})_2[\text{BF}_4]_2$	$\text{CD}_2\text{Cl}_2/295$	7.44, 4.68		137
$\text{Cu}_2(\mu\text{-}3)_2(\text{MeCN})_4[\text{BF}_4]_2$	$\text{CD}_2\text{Cl}_2/295$	7.69, 4.77		137
$\text{Cu}_2(\mu\text{-}3)_3[\text{BF}_4]_2$	$\text{CD}_2\text{Cl}_2/295$	4.63		137
$\text{Cu}_2(\mu\text{-}3)_3(\text{MeCN})[\text{BF}_4]_2$	$\text{CD}_2\text{Cl}_2/295$	5.45		137
$\text{Cu}_2(\mu\text{-}3)_3[\text{P}(\text{OMe})_3]_2[\text{BF}_4]_2$	$\text{CDCl}_3/293$	1.70		137
$\text{Cu}_2(\mu\text{-}3)_3(\text{PMe}_3)_2[\text{BF}_4]_2$	$\text{CDCl}_3/293$	1.46, -43.11		137
$\text{Cu}_2(\mu\text{-}3)_3(4\text{-Mepyr})_2[\text{BF}_4]_2$	$\text{CDCl}_3/293$	1.82		137
$\text{Cu}_2(\mu\text{-}3)_3(2\text{-Mepyr})[\text{BF}_4]_2$	$\text{CDCl}_3/293$	4.79		137
$\text{Cr}(\text{CO})_6(\text{C}_6\text{H}_5)$	CDCl_3	59.37		131
$\text{W}(\text{CO})_6(\text{C}_6\text{H}_5)$	CDCl_3	24.36	122.07 (J_{PW})	131
$\text{Cr}(\text{CO})_4(\text{C}_6\text{H}_5)_2$	CDCl_3	75.52		131
$\text{W}(\text{CO})_4(\text{C}_6\text{H}_5)_2$	CDCl_3	25.03		131
$\text{UO}_2(\text{NO}_3)_2[(\text{C}_6\text{H}_5)_2\text{PO}]_2\text{pyrO}$	$\text{CDCl}_3/300$	31.1		86
$\text{Ru}_3(\text{CO})_9(\text{C}_6\text{H}_5)_3$	CD_2Cl_2	37.7		22
$\text{Ru}_3(\text{C}_6\text{H}_5)_2(\text{CO})_3$	CD_2Cl_2	57.8		22
$\text{Ru}(\text{C}_6\text{H}_5)(\text{CO})_2\text{Cl}_2$	CD_2Cl_2	-6.8		22, 70
$\text{Ru}(\text{C}_6\text{H}_5)(\text{CO})_2\text{Cl}_2$	CD_2Cl_2	21.5		22
$\text{RuPd}(\text{C}_6\text{H}_5)_2(\text{CO})\text{Cl}_2$	CD_2Cl_2	38.9, 17.9, 20.1, 16.5		22
$\text{Ru}(\text{C}_6\text{H}_5)(\text{CO})_2\text{Br}_2$	CD_2Cl_2	-8.87		70
$\text{Ru}(\text{C}_6\text{H}_5)_2(\text{CO})_2\text{Cl}_2$	CD_2Cl_2	21.49		70
$\text{Au}(2\text{-pyrPMe}_2)\text{Cl}$	CDCl_3	-5.95		18
$\text{Au}[(2\text{-pyr})_2\text{PMe}]\text{Cl}$	CDCl_3	19.60		18
$\text{Au}[(2\text{-pyr})_3\text{P}]\text{Cl}$	CDCl_3	32.24		18
$\text{Au}[(2\text{-pyr})\text{P}(\text{C}_6\text{H}_5)_2]\text{Cl}$	CDCl_3	32.66		18
$\text{Au}[(2\text{-pyr})_2\text{P}(\text{C}_6\text{H}_5)]\text{Cl}$	CDCl_3	32.41		18
$\text{RuH}(\text{Cl})(\text{C}_6\text{H}_5)_3$	CD_2Cl_2	74.7		8
$\text{Ru}(\text{Cl})_2(\text{C}_6\text{H}_5)_2$	CD_2Cl_2	-0.3		8
$[\text{Ir}_2(\text{COD})_2(\text{NIPHOS})_2][\text{SbF}_6]_2$	CD_3CN	108.0		130
$[\text{Ir}_2(\text{NBD})_2(\text{NIPHOS})_2][\text{SbF}_6]_2$	$(\text{CD}_3)_2\text{CO}$	107.9		130
$\text{Ir}(\text{C}_6\text{H}_5)_2[\text{pyrCH}(\text{P}(\text{C}_6\text{H}_5)_2)_2][\text{BF}_4]$	CH_2Cl_2	9.6		129
$\text{Ir}_2(\mu\text{-CO})(\text{CO})_2[\text{pyrCH}(\text{P}(\text{C}_6\text{H}_5)_2)_2][\text{BF}_4]_2$	MeCOMe	28.1		129
$\text{Ir}(\text{CO})[\text{pyrCH}(\text{P}(\text{C}_6\text{H}_5)_2)_2][\text{BF}_4]$	CH_2Cl_2	~30		129
$\text{Ir}_2(\text{CO})_2(\text{I})[\text{pyrCH}(\text{P}(\text{C}_6\text{H}_5)_2)_2][\text{BF}_4]$	CH_2Cl_2	8.83, 18.5, 31.6, 39.2		129
$[\text{pyrP}(\text{C}_6\text{H}_5)_2\text{Fe}(\text{CO})_3]_2$	$\text{CD}_2\text{Cl}_2/298$	76.2		73
$\text{W}(\text{NIPHOS})(\text{CO})_5$	CDCl_3	160.5	273 ($^1J_{\text{PW}}$)	68
$\text{W}(\text{NIPHOS})(\text{CO})_4$	CDCl_3	205.2	271 ($^1J_{\text{PW}}$)	68
$\text{Cr}(\text{NIPHOS})(\text{CO})_5$	CDCl_3	208.6		68
$\text{Os}_3(\text{CO})_{10}(\mu\text{-}3)$	CD_2Cl_2	5.6		169
$\text{Os}_3(\text{CO})_{11}(\text{C}_6\text{H}_5)$	DCCl_3	4.2		169
$\text{Os}_3(\text{CO})_{10}(\text{C}_6\text{H}_5)$	CD_2Cl_2	12.7		169
$\text{Os}_3(\text{CO})_{10}(\mu\text{-}4)$	CD_2Cl_2	8.4		169
$\text{NiBr}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)[2\text{-pyrCH}_2\text{P}(\text{C}_6\text{H}_5)_2]$	$\text{C}_6\text{H}_5\text{Me}$	30		138
$\text{Zn}[2,6\text{-pyr}[\text{CH}_2\text{O}(\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2]_2](\text{CF}_3\text{SO}_3)_2$	CH_2Cl_2	-9.5		46
$\text{ZnCl}(\mu\text{-Cl})\text{Rh}(\text{CO})\{2,6\text{-pyr}[\text{CH}_2\text{O}(\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2]_2](\text{CF}_3\text{SO}_3)$	CH_2Cl_2	26.4	119	46
$\text{Cr}(\text{NIPHOS})(\text{CO})_4$	CDCl_3	249.6		68
	C_6D_6	247		68

^a NIPHOS (38) = 2-(2-pyridyl)-4,5-dimethylphosphorine.

Table 8. Crystal Structures of Pyridylphosphine Ligands and Complexes

crystal structures ^a	metal	bond distances (Å)			bond angles (deg)			distance (Å)		miscellaneous distances (Å) or angles (deg)	ref(s)
		M-P	M-N	M-X	X-M-P	N-M-P	M-M'-P	M-M'	P-C _{pyr}		
2-pyrP(C ₆ H ₅) ₂ (3)									1.837(3)	0.83(3)-0.99(3) [C-H] 115.7(2)-123.8(2) [C-C-H]	139
(2-pyr) ₃ P (5)									1.824(3) 1.826(2) 1.834(3)	102.7(1), 101.9(1), 101.0(1) [C-P-C]	140
2-pyrCH=PC ₆ H ₄ (t-bu) ₃										-177.7(8) [C7-P-C1-C2] -84.6 [C1-P-C7-C8]	64 64
PtMe(η ² -3)(3)[B(C ₆ H ₅) ₄]	Pt	2.325(5) 2.207(5)	2.07(2)			70.4(5) 176.5(4)			1.81(2)	2.05(2) [Pt-CH ₃]	71
Pt(3-PO)Br ₄	Pt		2.102(14)						1.812(18)	1.527(13) [P-O] 2.106(11) [Pt-O] 177.6(1) [Br-Pt-Br] 89.3(1) [Br-Pt-Br]	82
trans-Rh(CO)(Cl)(3) ₂ Rh ₂ (form) ₂ (μ-3)(CF ₃ CO) ₂	Rh Rh(1) Rh(2)	2.298(4) 2.267(1) 2.269(2)	2.050(4)-2.139(4) 2.139(4)	2.465(2) 2.471(2) 2.429(2) 2.404(2)				2.5406(6)	1.86(1) 1.834(6)	1.83 [Rh-CO] 2.407(4) [Rh-O] 2.327(4) [Rh-O]	141 142
(η ⁵ -C ₅ H ₅)Rh(μ-CO)(μ-3)- Rh(CO)Cl	Rh(1) Rh(2)	2.222(2)	2.107(8)	2.346(3) 2.630(1)				2.648(1)	1.877(9)	1.925(12) [Rh-Cp*] 1.847(8) [Rh-Cp*] 1.811(8) [Rh-CO]	143 143
(η ⁵ -C ₅ H ₅)Rh(μ-1)(μ-3)Rh(CO)I ₂	Rh(1) Rh(2)		2.153(5)	2.647(1) 2.812(1)				2.686(1)	1.832(6)		
RhPd(μ-3) ₂ (CO)Cl ₃	Rh Pd	2.243(3) 2.220(4)	2.16(1) 2.13(1)	2.399(3) 2.499(4)				2.594(1)	1.823(4)	1.82(1) [Rh-CO]	110, 121
PdMo(μ-3) ₂ (μ-CO)(CO) ₂ - Cl ₂ 0.5CH ₂ Cl ₂	Pd Pd	2.221(2)	2.113(5)	2.391(2) 2.165(6)				2.817(1)	1.835(4) 1.844(6)	176.88(6) [Mo-Pd-Cl] 158.26(5) [Cl-Mo-Pd]	112, 144
[(t-buNC) ₂ Cl ₃ Rh(μ-3)- Pd(μ-Cl)] ₂	Mo Rh Pd	2.559(2) 2.520(7) 2.185(6)	2.320(5) 2.10(2)	2.487(2) 2.520(7) 2.380(6) 2.388(7) 2.479(9)				2.612(3)	1.827(6) 1.82(3)		107
(C ₆ H ₁₂)Rh(μ-Cl)(μ-3)- PdCl ₂ -CH ₂ Cl ₂	Rh Pd		2.05(2)	2.399(8)				3.210(4)	1.93(3)		107
[(η ⁵ -C ₅ H ₅)Rh(μ-DMA)(μ-3)Rh- (CO)(μ-Cl)] ₂ -CH ₂ Cl ₂	Rh(1) Rh(2)	2.246(9)	2.133(4)	2.516(1) 2.670(1)				2.661(1)		1.919(9) [Rh-Cp*] 1.822(6) [Rh-CO]	145
Ru ₃ (μ-η ² -C(O)C ₆ H ₅)[μ-η ² - Ppyr(C ₆ H ₅)](CO) ₉	Ru(1) Ru(2) Ru(3)	2.220(1) 2.356(2) 2.385(2)	2.165(8)					2.821(1)		2.877(1) [Ru(1)-Ru(3)] 3.639(1) [Ru(2)-Ru(3)]	146
Ru ₃ [(μ-η ² -C(O)C ₆ H ₅)](μ-η ² - Ppyr(CO)) ₃ [P(C ₆ H ₅) ₃]	Ru(1) Ru(2) Ru(3) Pd	2.369(1) 2.405(1) 2.402(1) 2.2469(18) 2.2569(13)	2.158(3)					2.842(1)		2.883(1) [Ru(1)-Ru(3)] 3.671(1) [Ru(2)-Ru(3)] 106.36(4) [P-Ru(2)-P]	146
cis-Pd(4) ₂ Cl ₂	Pd			2.3573(14) 2.3485(22)	168.73(11) 83.91(6) 85.82(8)			1.835(13)		100.46(6) [P-Pd-P] 91.86(6) [Cl-Pd-Cl]	69
cis-Pd(4) ₂ Cl ₂ -C ₆ H ₆	Pd	2.2624(8) 2.2623(8)		2.3495(9) 2.3550(9)	167.87(8) 84.79(3) 170.87(5) 171.76(6) 87.54(3)			1.835(10)		96.69(2) [P-Pd-P] 92.18(3) [Cl-Pd-Cl]	69

Complex	Crystallographic Data	Ref.
<i>cis</i> -Pd(4) ₂ (2-pyrH)Cl ₂ -C ₆ H ₆	2.2433(8)	69
[Pd]([C ₆ H ₅) ₂ P(2,6)pyrP(O)-(C ₆ H ₅) ₂ Cl] ₂	2.228(2)	69
[(dpm)Rh(Cl)(CH ₂ pyrP(C ₆ H ₅)-(CH ₂) ₂ Ppyr(C ₆ H ₅))Cl+CH ₂ Cl ₂	2.206(1) 2.261(1) 2.520(2) 2.429(2) 2.541(2)	147
Re ₃ [μ ₃ -P(C ₆ H ₅) ₂](μ ^{-η⁴} -CHP(C ₆ H ₅)pyr)(CO) ₇	2.228(5)	148
Pd ₂ I ₂ (3) ₂ ·0.5C ₃ H ₆ O	2.121(4) 2.103(4)	111
Pd ₂ Cl ₂ (5) ₃ (μ-DMAD)·2CH ₂ Cl ₂	2.206(1) 2.2434(9) 2.128(3) 2.127(3)	111
Pd ₄ (2,6-pyr[P(C ₆ H ₅) ₂] ₃ -Cl ₆ ⁿ -CH ₂ Cl ₂	2.2260(9)	108
Rh ₃ Sn ₂ (CO) ₂ Cl ₆ [2,6-pyr-(P(C ₆ H ₅) ₂) ₂ ·2CH ₂ Cl ₂	2.349(5) 2.330(5)	149
[μ ₂ -2,6-pyr(P(C ₆ H ₅) ₂) ₂ Rh ₄ -(μ-CO) ₂ (CO) ₂ (μ-Cl) ₂ ·2CH ₂ Cl ₂ ·2N ₂	2.304(5) 2.288(6)	108, 149
[Rh ₂ [μ ₂ -2,6-pyr(P(C ₆ H ₅) ₂) ₂ ·(CO)(CH ₃ OH)Cl] ⁺	2.62(1) 2.42(1)	150
AuCl(3)	2.313(4) 2.314(4) 2.333(4) 2.329(4)	151
AuCl(5)	2.286(4) 2.214(4)	152
[Ru(5-PO)[2-pyr] ₂ P(O)O]-[BF ₄]-2H ₂ O	2.234(4) 2.277(5)	153
Zn(5)(NO ₃) ₂	2.04(3)-2.11(3)	154
Zn(5) ₂ [ClO ₄] ₂	2.050(3) 2.047(3) 2.253(3) 2.178(4) 2.152(4)	154
[Ru(5) ₂ (tos) ₂ -C ₂ H ₅ OH	2.06(1)-2.09(1)	155
<i>rac</i> -{[(C ₆ H ₅)pyrP] ₂ CH ₃ [Rh-(CO)Cl] ₂ ·2MeCN	2.212(2) 2.134(5) 2.148(5)	19
<i>meso</i> -{[(C ₆ H ₅)pyrP] ₂ (CH ₂) ₃]-Rh ₂ Cl ₃ [Rh(CO) ₂ Cl] ₂	2.219(2) 2.148(5) 2.336(4) 2.335(4) 2.511(2)	19
	2.244(3) 2.261(2) 2.185(7)	
	1.829(9) 1.812(12)	
	1.980(3) [Pd-Cl] 91.04(3) [Cl-Pd-Cl] 1.479(6) [P-O]	
	2.023(3) Rh-C 1.510(4) N-C(-Rh) 2.318(7) Re-CH 1.825(7) P-CH	
	only perspective drawing shown 173.2(2) [P-Rh-P] 97.5(2) [Cl-Rh-Cl] 1.85(2) [Rh-CO]	
	2.588(2) 2.587(2) 2.601(2) 2.588(2) 2.587(3)	
	1.92(2) [Rh-CO] 137.1(2) [P-Rh-P] 171.4(9) [N-Sn-N] 91.3(2) [Cl-Sn-Cl] 92.5(2) [Cl-Sn-Cl] 99.7(2) [Cl-Sn-Cl] 168.0(1) [Rh(1)-Rh(2)-Rh(2')]	
	2.921(2) 2.594(2)	
	5.425(2)	
	1.78(1) [Rh-CO] 1.809(16) [Rh-CO]	
	114.0(6) [Au-P-C] 114.4(6) [Au-P-C']	
	1.84(1)	
	1.80(2)-1.85(2) 1.837(6) 1.854(6) 1.829(9) 1.814(9)	
	3.093(1) 91.9(1) 93.4(1) 2.650(1) 174.8(2) 94.2(2) 175.9(2)	
	1.797(6) [Rh-CO] 1.808(6) [Rh-CO] 1.79(1) [Rh-CO] 1.81(1) [Rh-CO]	

Table 8 (Continued)

crystal structures ^a	metal	bond distances (Å)			bond angles (deg)		distance (Å)		miscellaneous distances (Å) or angles (deg)	ref(s)
		M-P	M-N	M-X	X-M-P	N-M-P	M-M'	P-C _{pyr}		
Rh ₂ [μ-12,6-pyr(P(C ₆ H ₅) ₂) ₂] ₂ (μ-CO)(μ-I)[B(C ₆ H ₅) ₄] ₂ CH ₂ Cl ₂	Rh(1)	2.292(4)	2.081(9)	1.859(2)	91.9(1)	176.1(3)	2.568(2)	1.834(13)	2.02 [Rh-CO] 107.4(1) [P-Rh-P] 2.04 [Rh-CO] 107.1(1) [P-Rh-P] 88.4(2) [Cl-Pt-Cl] 96.2(2) [P-Pt-P]	123
Pt ₂ [μ-(C ₆ H ₅) ₂ P] ₂ pyr ₂ Cl ₂ ·6CH ₂ Cl ₂	Pt	2.238(3)	2.106(10)	2.919(2)	93.8(1)	176.8(3)	2.577(2)	1.861(10)		77
Pt ₂ [μ-(C ₆ H ₅) ₂ P] ₂ pyr ₂ Cl ₂ ·6CH ₂ Cl ₂	Pt	2.251(4)	2.356(7)	2.363(7)	176.6(2)	69.7(3)		1.868(12)		77
Pt ₂ [μ-(C ₆ H ₅) ₂ P] ₂ pyr ₂ Cl ₂ ·6CH ₂ Cl ₂	Pt	2.252(7)	2.363(7)		86.5(2)			1.828(26)		77
Pt ₂ [μ-(C ₆ H ₅) ₂ P] ₂ pyr ₂ Cl ₂ ·6CH ₂ Cl ₂	Pt	2.278(7)			89.2(2)					77
Pt ₂ [μ-(C ₆ H ₅) ₂ P] ₂ pyr ₂ Cl ₂ ·6CH ₂ Cl ₂	Pt	2.307(4)	2.602(1)	2.607(1)	171.6(2)		1.840(18)			77
Pt ₂ [μ-(C ₆ H ₅) ₂ P] ₂ pyr ₂ Cl ₂ ·6CH ₂ Cl ₂	Pt	2.306(5)			93.2(1)					77
[Pt(3-Cl)[Rh(CO) ₂ Cl ₂]-0.5CH ₂ Cl ₂]	Pt	2.223(6)	2.07(2)	2.340(5)	166.8(2)	70.8(6)	1.84(2)	1.86(2)	91.7(2) [Cl-Rh-Cl] 1.79(2), 1.86(2) [RhCO]	113
Rh ₂ (3) ₂ (μ-CO)Cl ₂	Rh	2.232(6)		2.353(5)	92.2(2)	171.1(5)				113
Rh ₂ (3) ₂ (μ-CO)Cl ₂	Rh	2.206(1)	2.116(5)	2.342(6)	91.9(1)	172.0(1)	2.612(1)	1.831(6)	84.3 [Rh-C-Rh]	121, 124
Rh ₂ (3) ₂ (μ-CO)Cl ₂	Rh	2.215(1)	2.114(5)	2.355(1)	93.3(1)	177.8(1)				137
Cu ₂ (μ-3) ₂ (MeCN)[BF ₄] ₂	Cu(1)	2.196(2)	2.056(6)	2.355(1)	132.3(2)	127.7(2)	2.721(3)	1.842(6)		137
	Cu(2)	2.274(2)	2.048(4)		108.5(1)	116.6(1)	1.832(7)			137
	Cu(2)	2.310(3)	2.089(5)		97.7(2)					137
PtMo(μ-3) ₂ (μ-CO)(CO) ₂ Cl ₂ ·0.406CH ₂ Cl ₂	Pt	2.248(5)	2.301(17)	2.324(4)	95.5(2)	97.8(2)	2.845(1)		166.1(2) [P-Pt-P] 2.218(17) [Pt-CO] 1.907(20) [Mo-CO] 1.950(18) [Mo-CO] 1.954(17) [Mo-CO] 2.110(3), 2.116(3) [Mo-O] 1.96 [Mo-CO]	119
	Mo	2.227(5)	2.315(12)	2.521(4)	93.4(2)					119
Mo ₂ (3) ₂ (Cl) ₂ (AcO) ₂ ·2CH ₂ Cl ₂	Mo	2.5341(7)	2.240(2)	2.7544(7)	79.12(2)	165.72(8)	2.1900(3)	1.844(3)		156
Mo ₂ (7-C ₆ H ₅) ₂ (CO) ₄ (3) ₂ ·2Et ₂ O	Mo	2.412(6)					3.276(3)	1.83(2)		132
(<i>η</i> ⁵ -C ₅ H ₅)(<i>t</i> -BuNC)Rh(μ-3)Pd-	Rh	2.241(2)					2.631(1)	1.820(6)		115
(<i>t</i> -BuNC)(Cl)PF ₆ C ₆ H ₅ MeOH	Pd		2.112(6)	2.406(2)						157
PdW(μ-3) ₂ (μ-CO)(CO) ₂ Cl ₂	Pd	2.541(2)	2.281(6)	2.480(2)	90.73(6)	95.0(1)	2.8119(5)	1.839(7)	2.23(1) [Co-CO] 1.30(2) [P-O] 94.8(1) [N-Co-N] 116.2(1) [Cl-Co-Cl] 143.33(7) [Co-Co-Cl]	85
0.7CH ₂ Cl ₂	Pd	2.205(2)	2.142(6)	2.387(3)	91.4(2)	173.6(2)		1.853(7)		158
Co(3PO) ₂ Cl ₂	Co		2.134(5)	2.305(2)				1.835(7)		158
Co(4)Cl ₂ ·1/2EtOH	Co		2.134(5)	2.305(2)						159
Co(0)Co(I)(μ-3) ₂ (μ-CO)(CO)Cl	Co(1)		2.031(2)	2.221(1)			2.441(2)	1.873(8)		159
	Co(1)		2.137(7)	2.238(3)						159
	Co(2)		2.100(6)					1.867(8)		159
Co(II)Co(III)(μ-3) ₂ (μ-CO) ₂ Cl ₃	Co(1)	2.177(3)			94.1(4)		2.685(1)	1.83(2)		160
	Co(1)	2.182(2)			88.7(3)					160
	Co(2)	2.305(10)								160
	Co(2)	2.32(2)						1.84(3)		160
cis-Re ₂ (μ-AcO) ₂ Cl ₂ (μ-3) ₂ [PF ₆]	Re(1)	2.401(6)	2.248(14)	2.485(4)	83.6(2)	91.7(5)	2.261(1)			161
	Re(2)	2.406(5)	2.17(2)	2.506(5)	85.7(2)	97.7(4)				161
Re ₂ Cl ₃ (3) ₂ [(C ₆ H ₅)(C ₆ H ₄)Ppyr]	Re(1)	2.388(9)	2.13(1)	2.532(5)	85.3(3)	163.3(3)	1.80(3)-1.84(3)		85.0(3) [Cl-Re-Cl] 98.3(3) [P-Re-P]	23, 134
	Re(2)	2.359(10)	2.08(2)	2.578(9)	96.3(3)	98.1(7)	1.84(3)			23, 134
	Re(2)		2.429(9)		80.5(3)					23, 134
	Re(2)		165.3(3)							23, 134
	Re(2)	2.354(9)	2.17(3)	2.568(9)	82.8(3)	170.5(7)			2.16(3) [Re-C]	23, 134
	Re(2)		2.22(3)		92.1(6)					23, 134

$\text{Re}_2\text{Cl}_2(3)_4(\text{PF}_6)_2\text{Me}_2\text{CO}$	Re(1) 2.436(5) 2.429(5)	2.19(2) 2.210(15)	2.575(5)	86.3(2) 88.0(2)	91.1(4) 87.9(4) 88.1(2)	2.300(1) 1.82(2)–1.83(2) 1.83(2)	174.4(2) [P–Re–P] 169.5(6) [N–Re–N]	23
	Re(2) 2.428(6) 2.433(6)	2.18(2) 2.227(15)	2.628(6)	88.1(2) 86.0(2)	91.4(5) 87.2(4) 92.8(5)		174.0(2) [P–Re–P] 169.3(6) [N–Re–N]	
$\text{Re}_2\text{Cl}_4(3)_2(\text{PEt}_3)$	Re(1) 2.365(2) 2.480(3)	2.206(7)	2.616(2) 2.406(2)	77.50(8) 84.08(9) 165.40(8)	92.0(2) 162.9(2)	1.829(8)–1.84(9) 1.84(9)	89.65(8) [Cl–Re–Cl] 100.25(9) [P–Re–P]	23
	Re(2) 2.346(2)	2.076(7)	2.355(2)	85.07(5)	93.5(2)		85.1(1) [Cl–Re–Cl]	
$\text{Os}_2(\text{AcO})(3)_2\text{Cl}_4\cdot 2\text{CH}_2\text{Cl}_2$	Os(1) 2.329(5)	2.09(2)	2.387(2) 2.428(6)	87.30(9) 154.75(9) 83.6(2)	90.8(4)	1.82(2)	2.10(1) [Os–O] 87.9(2) [Cl–Os–Cl] 2.10(1) [Os–O] 88.6(2) [Cl–Os–Cl] 2.096(5) [Os–O] 86.91(8) [Cl–Os–Cl] 2.110(5) [Os–O] 88.42(7) [Cl–Os–Cl]	162
	Os(2) 2.331(6)	2.06(2)	2.377(6)	83.3(2)	90.2(1)	1.81(2)		
$\text{Os}_2(\text{AcO})(3)_2\text{Cl}_4\cdot 2\text{Me}_2\text{CO}$	Os(1) 2.332(2)	2.066(6)	2.365(6)	169.4(2)	90.6(2)	1.834(8)		162
	Os(2) 2.338(2)	2.060(6)	2.362(2) 2.436(2)	84.23(8) 169.13(7)	90.9(2)	1.831(8)		
$\text{Rh}_2(\text{AcO})_2(3)_2\text{Cl}_2$	Rh(1) 2.212(3)	2.046(10)	2.371(2)	170.16(8)	91.2(3)	1.853(11) 1.847(13) 1.82(1)		162
$\text{UO}_2(\text{NO}_3)_2[(\text{C}_6\text{H}_5)_2\text{P}(\text{O})]\text{pyrO}$	Rh(2) 2.220(3)	2.068(9)	2.538(3) 2.537(3)	97.8(1) 97.3(1)	90.9(3)		2.41(1) U–O(P) 2.38(1) U–O(N) 2.086(5) Mo–N(CS) 1.834(16) [Cl–Ag–Cl] 1.826(16) [Cl–Ag–Cl] 1.824(16) [Cl–Ag–Cl] 1.828(16) [Cl–Ag–Cl] 98.1(1) [Cl–Ag–Cl]	86 163 116 164
$\text{Mo}_2(\text{NCS})_4(3)_2\cdot 2\text{THF}\cdot 2(\text{C}_6\text{H}_5\text{CH}_3)$ $\text{Mo}_2[(\text{C}_6\text{H}_5)_2\text{Ppyr}(6\text{-O})]_4$ [Ag(3)Cl] ₄	Mo Mo Ag(1)	2.545(2) 2.288(5) 2.387(5)	2.538(5) 2.646(5) 2.586(4) 2.803(5) 2.646(4) 2.721(5) 2.628(4) 2.709(4) 2.618(2) 2.701(4)	138.9(2) 119.2(2) 132.2(2) 114.8(1) 125.8(1) 130.2(1) 130.6(1) 118.4(1) 110.0(1) 106.25(9) 112.70(9) 100.7(1)	96.2(2)	2.191(1) 2.103(1)		
	Ag(2)	2.396(5)	2.538(5)	138.9(2)	126.7(2)		100.23(1) [Cl–Ag–Cl]	
	Ag(3)	2.429(5)	2.646(5)	119.2(2)	91.1(1)	1.836(6)		22
	Ag(4)	2.404(5)	2.721(5)	114.8(1)	167.3(1)	1.838(6)		
	Ag(1)	2.432(3)	2.618(2)	130.2(1)	68.7(2)	1.859(8)	1.877(8), 1.874(8) [Ru–CO]	70
	Ag(2)	2.452(3)	2.709(4)	130.6(1)	88.8(1)			
$\text{Ag}_2(3)_3\text{Cl}_2$	Ag(2)	2.436(4)	2.638(4)	112.1(1)	176.1(5)	1.83(2)	87.1(1) [Au–Au–P] 115.3(7) [Au–P–C] 73.8(1) [Pt–P–Rh] 88.0(4) [N–Rh–N] 110.4(1) [P–Rh–P] 102.5(1) [P–Rh–P] 105.9(1) [P–Rh–P]	151 18 127
$\text{RuPd}(3)_2(\text{CO})_2\text{Cl}_2\cdot 1.25\text{CH}_2\text{Cl}_2$	Ru	2.396(2)	2.601(9)	107.4(1)				
	Pd	2.190(2)	2.477(2)	100.6(1)				
$\text{Ru}(3)(\text{CO})_2\text{Cl}_2$	Ru	2.322(2)	2.408(2)	99.4(1)				
	Au	2.215(6)	2.417(2)	88.8(1)				
$[\text{Au}(2\text{-pyrPMMe}_2)]_2[\text{BF}_4]$	Pt	2.324(3)	2.287(3)					
$\text{PRh}[\mu\text{-P}(\text{C}_6\text{H}_5)_2](\mu\text{-pyrCH}[\text{P}(\text{C}_6\text{H}_5)_2]_2\text{-pyrCH}_2\text{P}(\text{C}_6\text{H}_5)_2)(\text{P}(\text{C}_6\text{H}_5)_3)[\text{BF}_4]_2$	Rh	2.276(3) 2.381(3) 2.282(3)	2.19(1) 2.12(1)					

Table 8 (Continued)

crystal structures ^a	metal	bond distances (Å)			bond angles (deg)			distance (Å)		miscellaneous distances (Å) or angles (deg)	ref(s)
		M-P	M-N	M-X	X-M-P	N-M-P	M-M'	M-M'	P-C _{pyr}		
{Rh ₂ [pyrCH(P(C ₆ H ₅) ₂) ₂ (CO) ₂][PF ₆] ₂ C ₃ H ₆ O	Rh	2.271(1) 2.358(1)	2.187(5)			77.2(1) 99.5(2)	3.054(1)			1.819(6) [Rh-CO] 1.76.70(6) [P-Rh-P] 1.74.0(2) [P-Rh-P] 1.14.5(2) [Rh-P-Zn] 2.22(1) [Zn-O] 2.23(1) [Zn-O] 1.72.0(2) [P-Ir-P] 1.71.3(2) [P-Ir-P]	129 46
Rh(CO)ZnCl(μ-Cl) ₂ (2,6-pyr[CH ₂ O- (CH ₂) ₂ P(C ₆ H ₅) ₂](CF ₃ SO ₃)	Rh	2.331(5) 2.325(4)		2.399(4)	91.4(2) 89.8(2)		4.002(1)				
Ir ₂ (μ-CO)(CO) ₂ [pyrCH(P(C ₆ H ₅) ₂) ₂][BF ₄] ₂	Ir(1) Ir(2)	2.319(5) 2.348(5)	2.32(1) 2.32(1)	2.360(4) 2.201(6)		77.2(1) 100.3(4)	2.815(1)				129
RhAu[pyrCH(P(C ₆ H ₅) ₂)[BF ₄ NO ₃]	Rh	2.325(5) 2.207(7) 2.227(6)	2.18(2) 2.14(2)			100.0(4) 176.1(5) 174.9(7) 77.5(7) 78.9(6)	2.850(2)			103.9(3) [P-Rh-P] 99.9(80) [N-Rh-N] 1.70.3(3) [P-Au-P]	128
Rh ₂ (CO)[μ-pyrCH(P(C ₆ H ₅) ₂) ₂] ₂ [B(C ₆ H ₅) ₄] ₂ ·2CH ₂ Cl ₂	Au Rh(1) Rh(2)	2.295(6) 2.285(7) 2.297 2.318 2.238 2.228				174.6(3) 173.4(3) 77.1(3) 82.5(3)	2.674(1)			1.72.5(2) [P-Rh-P] 1.78 [Rh-CO] 1.02.1(2) [P-Rh-P]	126
Ni(3) ₂ (CO) ₂	Ni	2.213(1) 2.220(1)								1.846(4) 1.839(5) 1.836(10) 1.826(10) 1.850(10) 1.835(13)	165 165 97
Ni[P(2,6-pyrCH=NO) ₃ BF][BF ₄]	Ni	3.452(3)	2.030(21) ^b 2.043(20) ^c							3.089(11) [Ni-B] 1.376(17) [B-F] 3.035(12) [Fe-B] 1.362(18) [B-F] 1.811(23) 1.823(26) 1.928(25) 1.854(10) 1.837(9) 1.842(9)	99, 166 100, 167
Fe[P(2,6-pyrCH=NO) ₃ BF][BF ₄]-CH ₂ Cl ₂	Fe	3.445(03)	1.931(11) ^b 1.978(06) ^c							3.078(15) [Zn-B] 1.383(16) [B-F]	168
Co[P(2,6-pyrCH=NO) ₃ BF][BF ₄]-CH ₃ CN	Co	3.428(8)	2.063(18) ^b 2.118(36) ^c							1.928(7), 1.889(7) [Cr-CO] 1.825(6), 1.843(6) [Cr-CO]	68
Zn[P(2,6-pyrCH=NO) ₃ BF][BF ₄]	Zn	3.399(3)	2.099(18) ^b 2.071(22) ^c			76.7(1)				74.1(1), 74.2(1) [Ir-P-Ir]	130
Cr[NIPHOS](CO) ₄	Cr	2.280(1)	2.193(4)								68
[PtCl(NIPHOSH-OMe)(PMe ₃)](SbF ₆)	Pt	2.189(1) 2.250(1)	2.153(4)	2.354(1)	71.6(05) 87.5(05)	83.8(11) 170.6(11)					79
[Ir ₂ (COD) ₂ (NIPHOS) ₂](SbF ₆)	Ir(1) Ir(2)	2.424(2) 2.377(4) 2.424(4)	2.128(12) 2.098(12)			80.6(3) 86.3(3) 86.3(3) 80.8(3)	2.894(1)				130
Os ₃ (CO) ₁₀ (μ-3)	Os(1) Os(2) Os(3)	2.371(3) 2.380(4)	2.22(1)							1.92(2) [Os-CO] 1.872(2) [Os-CO] 2.01(2), 1.94(2) [Os-CO] 1.825(5), 1.843(5) [Cr-CO] 1.889(7), 1.928(7) [Cr-CO]	169
Cr(NIPHOS)(CO) ₄	Cr	2.280(1)	2.193(4)			76.7(1)					130

^a Abbreviations: form, *N,N'*-di-*p*-tolylformamidinate; DMA or DMAD, dimethyl acetylenedicarboxylate; dpm, dipivalylmethanate or 2,2,6,6-tetramethylheptanedioate; NIPHOS (38), 2-(2-pyridyl)-4,5-dimethylphosphorin. ^b M-N(aldoxime) bond. ^c M-N(pyridyl) bond.

It is hoped that this review will afford a historical insight so that new ligand systems can be designed and constructed on the basis of the unique chemistry of pyridylphosphines.

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VI. Note Added In Proof

(*SP*-4-3)-{2-[(C₆H₅)₂PCH₂]C₅H₄N}{[(1,2,3- η)-3-(CH₂=CHCMe₂)]Pd[BF₄]} was prepared and shown, via NMR spectral data, to isomerize in solution.¹⁷⁹

When 5 was treated with [Ru₃(CO)₁₂] at room temperature in THF and a catalytic amount of N{[P-(C₆H₅)₃]₂Cl} was added, {Ru₃(μ -2-pyr)[μ -3-(2-pyr)₂-P](CO)₉} was formed. The proposed intermediates [Ru₃(CO)_n](5) (*n* = 10 and/or 11) decarbonylated and the 2-pyridyl moiety underwent a P → Ru migration. The use of 4, instead of 5, gave similar results, in which phenyl and 2-pyridyl moieties migrate in almost equal quantities. The mechanism of these results still needs to be determined.¹⁸⁰

Treatment of [Pt(3)(C₆H₅C≡C)₂] with 2 equiv of [Cu (or Ag) (MeCN)₄]⁺ afforded {Pt(3)(C₆H₅C≡C)₂-[Cu(MeCN)₂]₂}[PF₆]₂ or {Pt(3)₂(C₆H₅C≡C)₂-[Ag(MeCN)₂]₂}[PF₆]₂ in high yield; their photophysics and electrochemistry have been determined.¹⁸¹

Reaction of [Rh₂(μ -CO)Cl₂(3)₂] with NaBH₄ gave Rh₂(μ -CO)(BH₄)₂(3)₂, which was characterized by a crystal structure and shown to catalyze ethylene hydrogenation.¹⁸²

Bifunctional 2-[(C₆H₅)₂P(O)CH₂](C₅H₄N(O)) and trifunctional 2,6-[(C₆H₅)₂P(O)CH₂]₂C₆H₃N(O) have been prepared and several f-element [Pr^{III}, Tb^{III}, Yb^{III}, Th^{IV}] ion complexes have been created and confirmed by X-ray crystal data.¹⁸³

Treatment of [Rh(COD)Cl]₂ with 2-pyr(CH₂)₂P-(C₆H₅)(CH₂)₃Y [Y = OEt; OC₆H₅; NHC₆H₅; NHC₆H₁₁] in the presence of TlPF₆ (a halogen scavenger) at 0 °C gave {Rh(COD)[2-pyr(CH₂)₂P(C₆H₅)(CH₂)₃Y][PF₆]}₂, which catalytically polymerizes phenylacetylene to polyacetylene with improved selectivity and larger *M_w* values over previous catalysts.¹⁸⁴

An [Os₃(CO)₁₀(μ -3)] cluster possessing a diaxially coordinated 3 bridge reportedly undergoes pyridine transfer between two metal atoms, whereas the *P*-atom forms a strong bond to the third metal atom.¹⁸⁵

Treatment of *cis*-[Pt(DMSO)₂Cl₂] with 3 afforded *cis*-[Pt(DMSO)(3)Cl₂], which possesses a square planar Pt^{II} center and an η^1 -P-Pt bond. *cis*-[Pt(DMSO)(3)Cl₂] with an equimolar quantity of *cis*-[Pt(DMSO)₂(Me)₂] gave the binuclear [(Me)ClPt(μ -Cl)(μ -3)Pt(Me)(DMSO)](DMSO) and [Pt₂(μ -

3)₂Cl₂](DMSO) complexes, which have been supported by X-ray data.¹⁸⁶

Treatment of {Fe(CO)₄(H)[Si(OMe)₃]} with 3 gave (75 %) [Fe(CO)₃[Si(OMe)₃](3)]. Reaction of K[Fe(CO)₃-[Si(OMe)₃](3)] with CdBr₂ afforded [(MeO)₃Si](CO)₃-Fe(μ -3)₂Cd(μ -Br)₂, which with 4-picoline gave {[MeO)₃Si](CO)₃Fe(μ -3)CdBr(4-pic)}], whereas K[Fe(CO)₃[Si(OMe)₃](3)] with CdBr₂ afforded *mer*-{[(MeO)₃Si](CO)₃Fe(μ -3)₂Cd}.¹⁸⁷

The acyl complex Ru₃[μ -C(O)(C₆H₅)] [μ -3- η^2 -P(C₆H₅)(2-pyr)](CO)₉ with 3 equiv of PH(C₆H₅)₂ and Ru₃[μ -3- η^2 -P(C₆H₅)(2-pyr)] [μ -P(C₆H₅)₂](CO)₆(μ -CO)₂ with 2 equiv of PH(C₆H₅)₂ both gave Ru₃[μ -3- η^2 -P(C₆H₅)(2-pyr)] [μ -P(C₆H₅)₂]₃(CO)₆, by the incorporation of a [(C₆H₅)₂P] moiety into the triruthenium complex shell which contained a face-bridging pyridylphosphine ligand; the structure was supported by X-ray data.¹⁸⁸

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