Pyridylphosphines

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Contents

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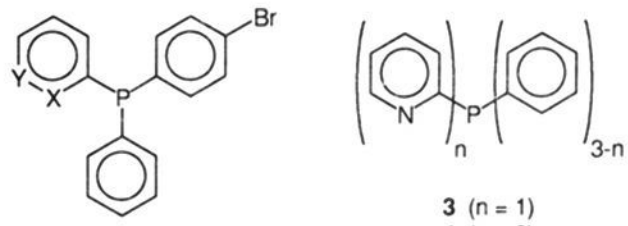
I. Introduction

The general preparation of phosphines has recently been overviewed[1] 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 presented[2] 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 similarly[2] the only known, to the best of my knowledge,[4] 3-pyridylphosphine **2** was prepared in a poor 7% yield.

Scheme 1



1 (X = N; Y = CH)
2 (X = CH; Y = N)

3 (n = 1)
4 (n = 2)
5 (n = 3)

The tri-2-pyridylphosphine (**5**) was prepared (13%) from 2-pyridylmagnesium bromide with PCl_3, whereas in 1948, this procedure was extended[5] to the synthesis of **3** and **4**. Numerous modifications of this general approach have appeared[6,79,156] 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 exchange[9] 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-

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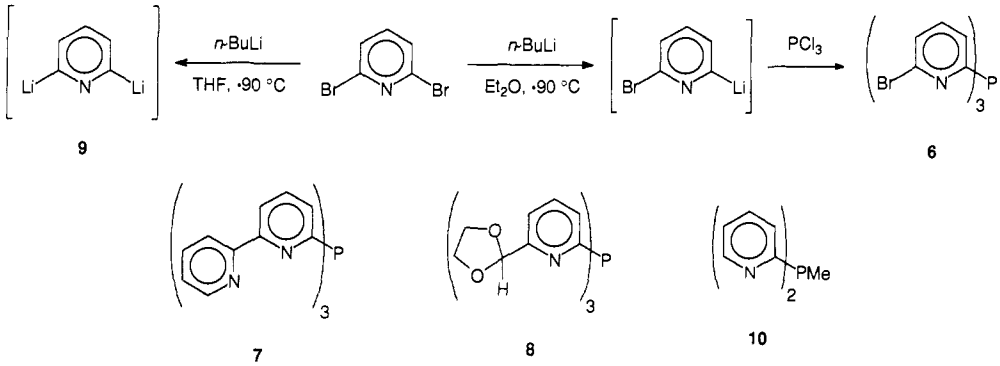
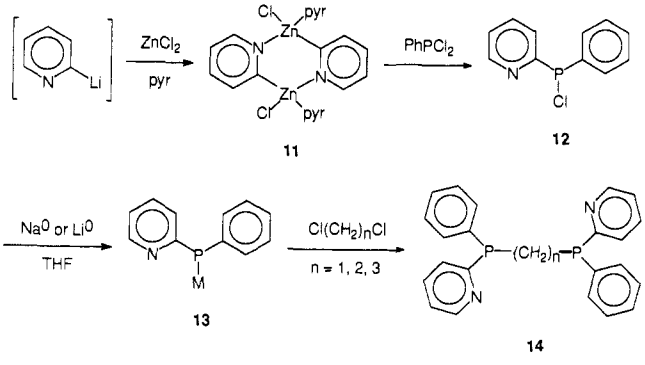
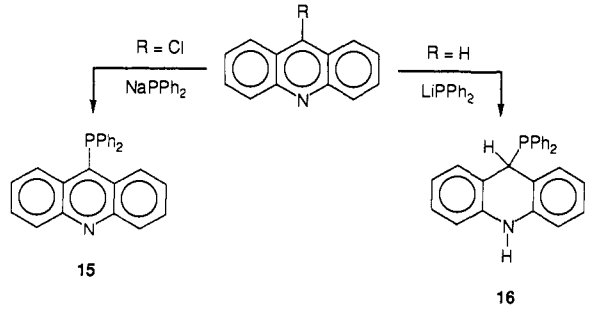
Scheme 2



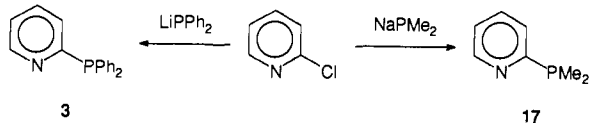
Scheme 3



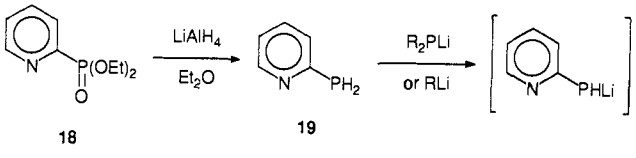
Scheme 4



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 prepared[12] by reaction of the appropriate pyridyllithium with PCl_3 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]

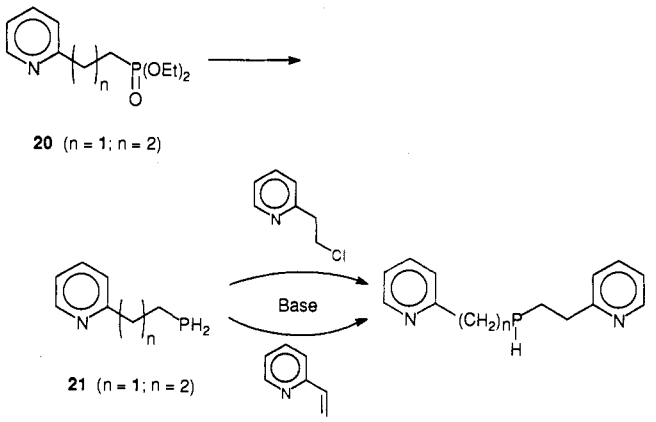
The addition of 2-lithiopyridine to several chlorophosphines was later repeated[17] to generate **3** (44%), **4** (39%), and **5** (20%). Diphenyl-4-pyridylphosphine was similarly prepared[81] (39%) by the reaction of 4-lithiopyridine with chlorodiphenylphosphine. The alkyl 2-pyridylphosphine **10** was prepared (43%) by using methyl dichlorophosphine.[18] Bis(pyridylphosphines) were prepared[19] 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 Na^0 ("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 Li^0 in this reduction is quicker but gives rise to less pure products.

In 1965, direct nucleophilic substitution by phosphide on pyridine occurred[20] since when 9-chloroacridine was treated with $KP(C_6H_5)_2$ in dioxane, phosphine **15** resulted (48%); whereas, when unsubstituted acridine was treated with $LiP(C_6H_5)_2$, the dihydro derivative **16** was formed in 31% yield (Scheme 4).

This general procedure was extended[21] 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 $LiP(C_6H_5)_2$, generated from diphenylphosphine with butyllithium in THF at 20 °C, gave excellent (94%) yields of **3**. Modification[23] of this procedure and the analogous reaction with $NaP(C_6H_5)_2$ have been reported;[24] whereas with $NaP(CH_3)_2$, **17** has been formed (62%)[18] (Scheme 5). When McFarlane et al.[25,26] treated 2,6-difluoropyridine with $NaP(C_6H_5)_2$ 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 $LiP(C_6H_5)_2$ 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 $LiAlH_4$ gave (ca. 80%) the related 2-pyridylphosphine (**19**)[29] (Scheme 6). Selective abstraction of protons from **19** and/or $(C_6H_5)PH_2$ or $(C_6H_5)_2PH$ 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



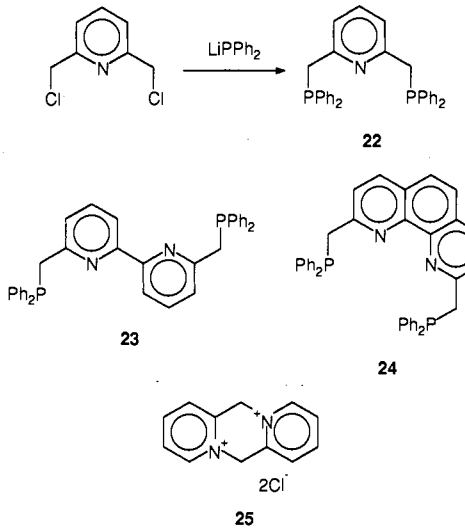
useful mono- and bidentates, and it readily, but reversibly, undergoes a Michael addition to α,β-unsaturated esters, including dimethyl vinylphosphonate. This reduction of pyridylphosphonates with $LiAlH_4$ should be applicable to other interesting esters, such as diethyl 4-pyridylphosphonate,[30] dimethyl [(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 prepared[36] 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 procedure[42] for 2-pyr$(CH_2)_2P(C_6H_5)_2$ was recently presented;[45] however, the advantages were not obvious. DuBois et al. reported[75] the free-radical addition of phenylphosphine to 2-vinylpyridine in the presence of AIBN under irradiation to afford [2-pyr$(CH_2)_2]_2P(C_6H_5)$, 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 $(C_6H_5)_2$-PH, gave (91%) 2,6-pyr$[CH_2O(CH_2)_3P(C_6H_5)_2]_2$.[46]

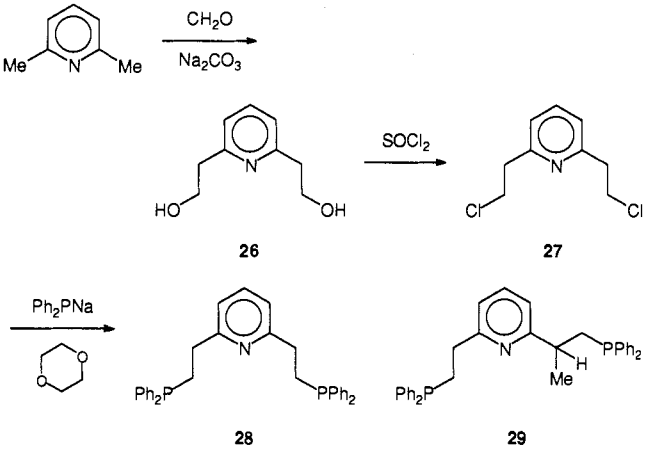
Simple nucleophilic substitution[47] of α-chloromethylheteroaryls with lithio or potassio diphenylphosphide (ref 48 and 49, respectively) under strictly air-free conditions has been shown to give variable yields (54–94%) of diverse pyridines **22** and **23** as well as pyridine-related bisphosphines (**24**) (Scheme 8). Speigel and Stetzer reported[36] that 2-(chloromethyl)pyridine dimerized to give 6,12-dihydrodipyrido[1,2-a:1′,2′-d]pyrazinediylium dichloride (**25**), which with $LiP(C_6H_5)_2$ gave the known[50] dipyrido[1,2-a:1′,2′-d]pyrazine. However when 2-(chloromethyl)pyridine was treated with C_6H_5-PHNa in THF at −78 °C exchange occurred to afford (74%) 2-pyr$CH_2PH(C_6H_5)$; whereas using C_6H_5PHLi, $(2\text{-pyr}CH_2)_2$ was formed.[36]

2,6-Bis[2-(diphenylphosphino)ethyl]pyridine (**28**) was prepared[51] 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 Loffler and Theil.[52] Conversion of (impure) **26** to the corresponding chloride **27** was conducted (50%) by treatment with thionyl

Scheme 8



Scheme 9



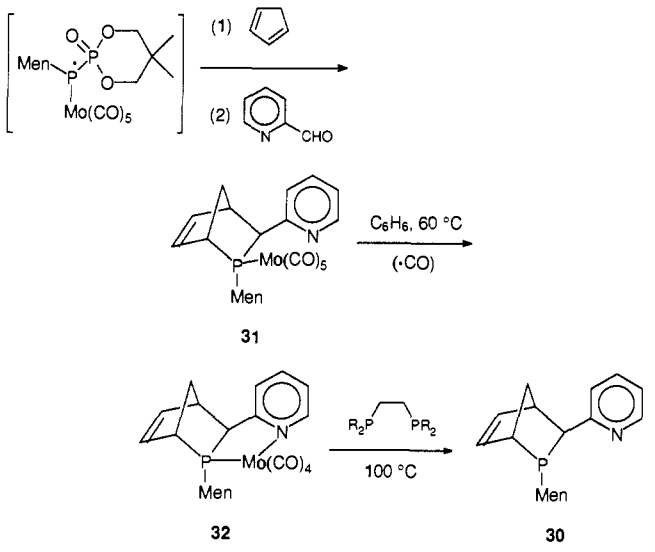
chloride. By using the general procedure of Issleib,[53] **27** with $NaP(C_6H_5)_2$ was transformed (23.8%) to the symmetrical diphosphine **28**. Also isolated was the unsymmetrical **29**, which was derived from the original impurities in starting material **27**.

Recently, an approach to chiral pyridylphosphine ligand **30** has been reported.[54] Complex **31** was prepared from the phospha-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.

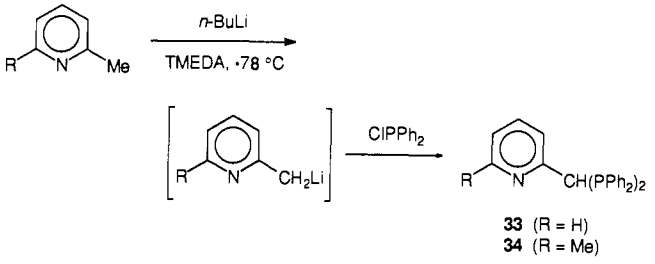
The use of the Arbuzov reaction to prepare phosphinoacetonitriles[55] has been recently applied to the synthesis of (pyridylalkyl)dialkylphosphines.[56,57] Although $LiAlH_4$ can be used in the reduction of the pyridylphosphoryl intermediates, silanes are recommended in this procedure when sensitive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

The preparation of 2-[bis(diphenylphosphino)methyl]pyridine (**33**) was reported,[59] but the preferred method of synthesis[60] of **33** was by the generation of 2-(lithiomethyl)pyridine at −78 °C and subsequent addition to $(C_6H_5)_2PCl$ (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 $(C_6H_5)_2PCl$ and subsequent

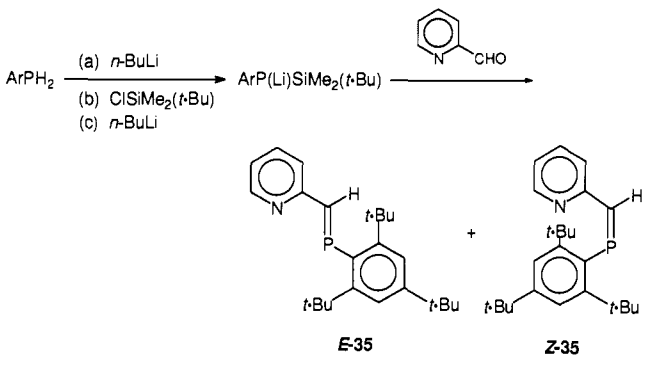
Scheme 10



Scheme 11



Scheme 12



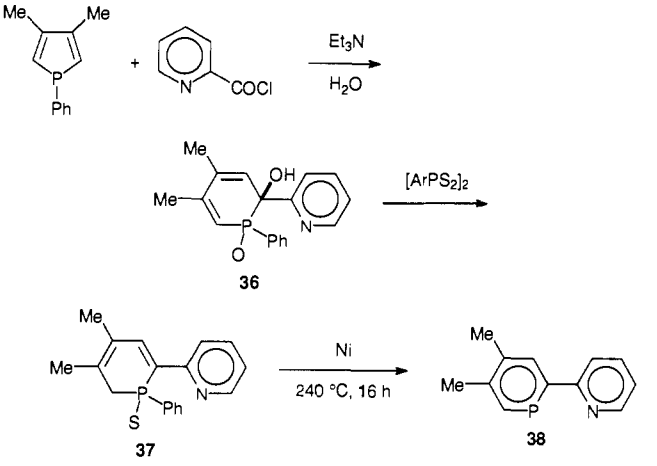
oxidation afforded low yields (ca. 21–26%) of the corresponding 4-substituted *P*-oxides.[63]

Pyridylphosphaalkenes[64] (**35**) were prepared from the appropriate pyridinecarboxaldehyde and ArP(Li)-$SiMe_2t$-bu, where Ar is 2,4,6-tri-*tert*-butylphenyl, via the procedure of Yoshifuji et al.[65,66] (Scheme 12). These phosphaalkenes 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 pK_a (5.25) for pyridine and the inability to measure a pK_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 trismethiodide **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*-derivatives[25] **44** (Scheme 14).

Scheme 14

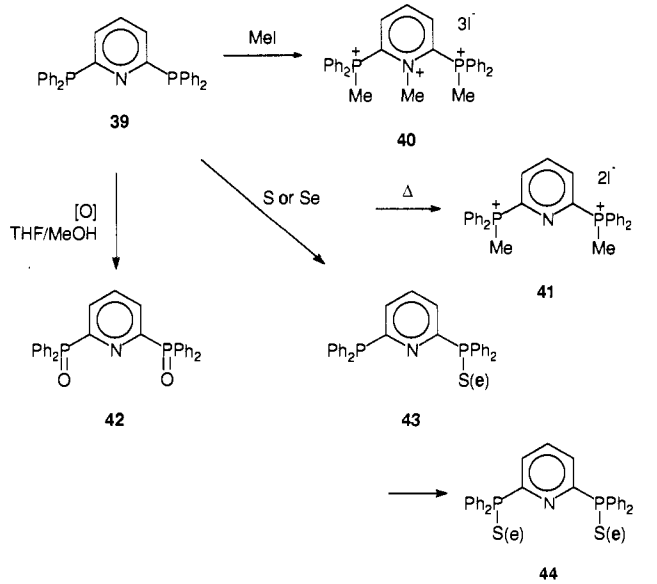


Table 1. ^{31}P NMR Data for the Ligands

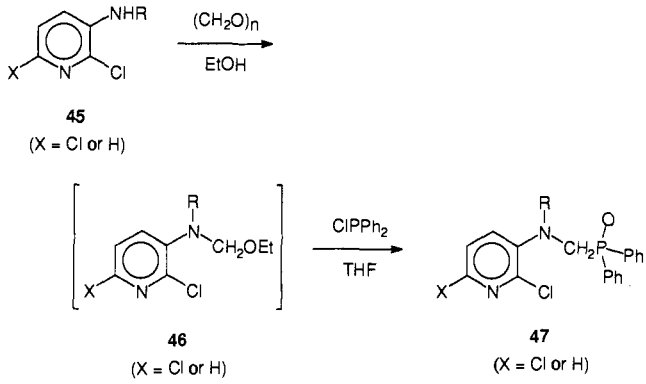
pyridylphosphine	solvent	δ (ppm)	^1J (PH)	ref(s)
2-pyrPH$_2$		−121.4	203	29
2-pyrPHD		−124.3	204, 32 ($^1J_{PD}$)	29
2-pyrPD$_2$		−127.0	32 ($^1J_{PD}$)	29
2-pyrPH(SiMe$_3$)	*t*-BuOMe	−118.6	194	29
2-pyrP(SiMe$_3$)$_2$	*t*-BuOMe	−125.1		29
(2-pyrPH)$_2$CH$_2$	DMF	−50.9, −54.8	223	29
2-pyrPHMe	DMF	−70.7	206	29
2-pyrPMe$_2$	CH_2Cl_2	20.6		29
	C_6D_6	41.62		18
2-pyrPMe$_3$(I$^-$)	CF_3CO_2H	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$_2$)	$C_6D_5CD_3$	13.06		18
2-pyrPH$_2$·*N*-MeI	CH_2Cl_2	−130.2	218	29
2-pyrPH$_2$·*N*-HCl	CH_2Cl_2	−132.4	216	29
2-pyrPH(CMe$_2$CH$_2$COMe)	*t*-BuOMe	−9.0	215	29
2-pyrPH(CH$_2$CH$_2$CO$_2$Me)	*t*-BuOMe	−49.6	210	29
2-pyrPH(CH$_2$CHMeCO$_2$Me)	*t*-BuOMe	−57.1, −58.3	211, 210	29
2-pyrPHCH(C$_6$H$_5$)CH$_2$CO$_2$Me	*t*-BuOMe	−23.3, 25.2	214, 210	29
2-pyrPH(CH$_2$)$_2$PH$_2$	*t*-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_2Cl_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$_5$)$_2$(*N*-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_6D_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(CClH$_2$)(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(*t*-Bu)	neat	−26.5	189	36
2-pyr(CH$_2$)$_2$PH(*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_6D_6	2.8		36
2-pyrCHPH(C$_6$H$_5$)(OSiMe$_3$)	Et$_2$O	−21.2, −33.1	217, 211	36
2-pyr(CH$_2$)$_2$PHSiMe$_3$	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-pyr)P]$_2$CH$_2$	$CDCl_3$	−19.2	>30 (J_{PP})	19
[(C$_6$H$_5$)(2-pyr)PCH$_2$]$_2$	$CDCl_3$	−10.4	≈35 (J_{PP})	19
[(C$_6$H$_5$)(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 ($^1J_{PSe}$)	25
2,6-[(C$_6$H$_5$)$_2$P(Se)]$_2$pyr		31.6	741 ($^1J_{PSe}$)	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_2O	−22.52		78
E-(2-pyrCH=PAr)	$CDCl_3$	285.41		64
Z-(2-pyrCH=PAr)	$CDCl_3$	259.6		64
E,E-[2,6-pyr(CH=PAr)$_2$]	$CDCl_3$	283.01		64
E,Z-[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$_5$)$_2$]$_2$	CH_2Cl_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-dimethylphosphorin.

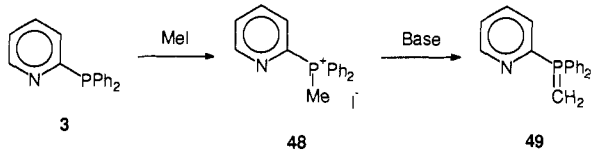
Table 2. ^{31}P NMR for the Lithiopyridylphosphines

lithiopyridylphosphines	solvent	δ (ppm)	^1J(PH)	ref
2-pyrPHLi	*t*-BuOMe	−96.6	195	29
2-pyrPLi(SiMe$_3$)	*t*-BuOMe	−112.7		29
2-pyrCH$_2$PLi(C$_6$H$_5$)	THF-Me	−46.9		36
2-pyr(CH$_2$)$_2$PHLi	THF-Me	−162.2	155	36
2-pyr(CH$_2$)$_2$PLi(C$_6$H$_5$)	THF-Me	−58.5		36
2-pyr(CH$_2$)$_2$PLi(*t*-Bu)	THF-Me	−27.3		36
2-pyr(CH$_2$)$_2$PLi(*i*-Pr)	THF-Me	−40.1		36

Scheme 15



Scheme 16



Halogenated 3-[*N*-alkyl-*N*-[(diphenylphosphinoyl)-methyl]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 (C$_6$H$_5$)$_2$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 methide[17] (Scheme 16).

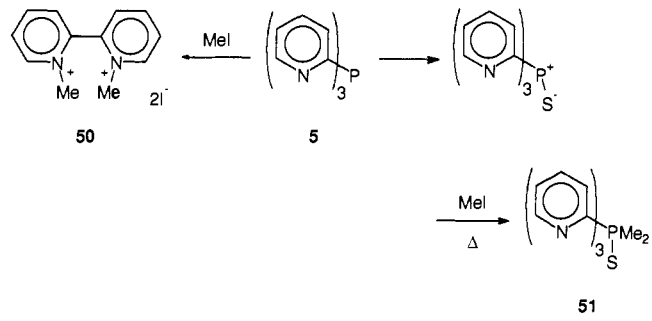
B. Fragmentation Reactions

Unusual fragmentations of pyridylphosphine derivatives were first noted[2] 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 found[5] 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.

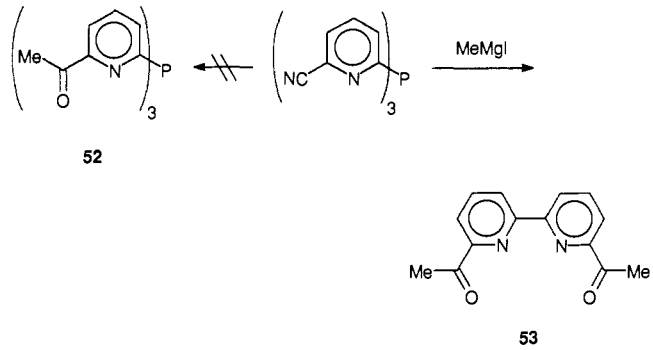
During his attempted synthesis of tris(6-acetylpyridinyl)phosphine (**52**), Parks[14] discovered that addition of methylmagnesium iodide to the corresponding trisnitrile gave predominantely 6,6′-diacetyl-2,2′-dipyridine (**53**) via a similar expulsion process (Scheme 18).

More recently during the preparation of pyridylphosphine macrocycles, Newkome and Hager[89] treated ligand **55** with alkoxide and isolated not the desired

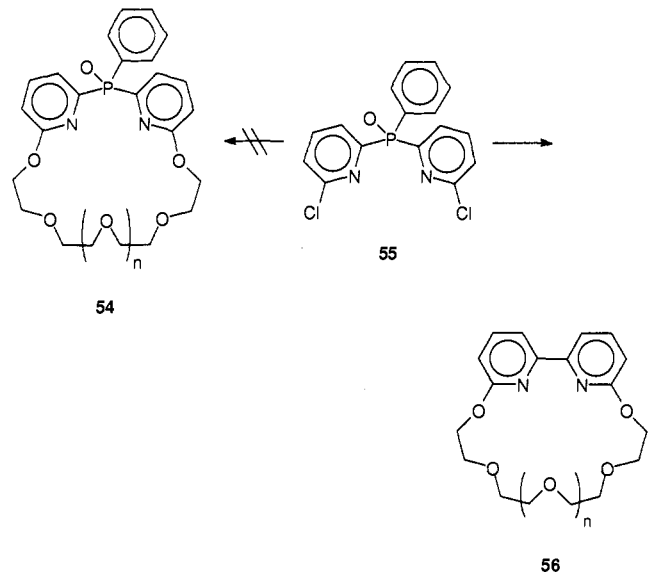
Scheme 17



Scheme 18



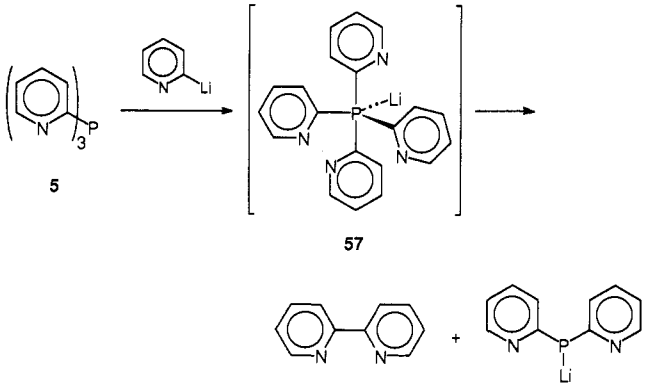
Scheme 19



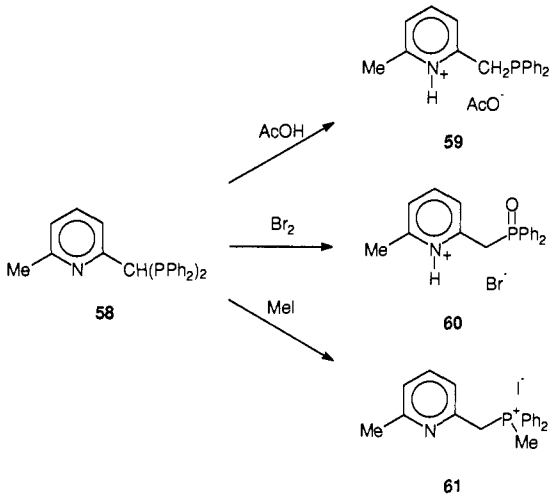
P-macrocycle **54** but rather **56**, which was free of phosphorus (Scheme 19). It was demonstrated[89] that *P*-oxides readily undergo a benzylic acid like rearrangement with the extrusion of a phosphorus moiety, whereas the parent phosphine of **55** was smoothly converted (47%) to the desired *P*-macrocycle. Further treatment of *P*-oxide **55** with sodium gycolate at 90–100 °C in toluene afforded (32%) the ring-contracted **56**. The proposed[89] 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 ketones[92] 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



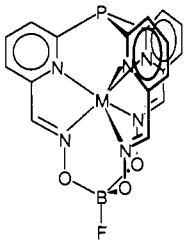
isolated in 81% yield. This transformation was rationalized as nucleophilic attack of the heteroaryllithium,[93] or more generally an organometallic[94] reagent on the phosphorus atom to generate a pentacoordinate intermediate **57**, from which the equitorial group couples with the axial substituent 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 reviewed[96] the ligand-coupling reactions of hypervalent specie 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 reported[42] the preparation of Ni(II), Co(II), Zn(II), and Cu(I) complexes of 2-pyr$(CH_2)_2P(C_6H_5)_2$. 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



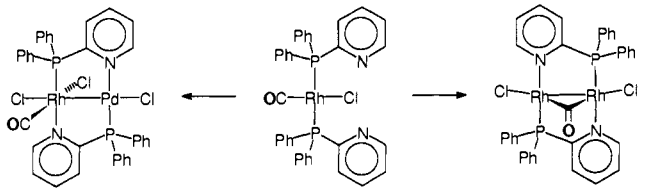
The first pivotal point in better understanding the complexation of pyridylphosphines was the rapid acquisition of X-ray crystallographic data. The earliest example was reported by Park, Wagner, and Holm in their 1970 communication,[10] when they synthesized hexacoordinate complexes possessing nonoctahedral 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, ^{19}F 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 Reis[97] had completed a single-crystal X-ray study of {Ni[P(2,6-pyrCH=NO)$_3$BF](BF$_4$)} (**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]

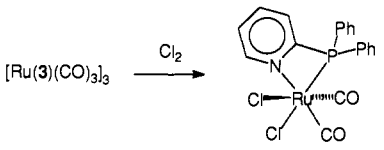
The second major breakthrough in the chemistry of pyridylphosphines came when NMR spectral information became readily available for phosphorus (^{31}P) and other metal centers (e.g., ^{195}Pt), thus permitting a quick snapshot of the *P*-center as well as dimagnetic metal center(s). This was especially 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 ^{31}P 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



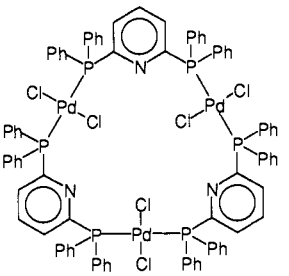
65 63 64

Scheme 24



66

Scheme 25



67

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 $Rh_2(\mu\text{-}Cl)(CO)_4$ to **3** generated the *P,P'*-complex **63**, which with an additional equivalent of $Rh_2(\mu\text{-}Cl)_2(CO)_4$ was converted to $Rh_2(\mathbf{3})_2(\mu\text{-}CO)(Cl_2)$ (**64**), although with Pd(COD)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 $[Ru(\mathbf{3})(CO)_3]_3$ 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 possible[70] (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 $[Rh(CO)_2Cl]_2$ 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 $[Rh_2(CO)_4Cl_2]$ 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 reorganization[150] of **69** to **70** in which two rhodium atoms have been eliminated; treatment of **70** with $Rh(\mu\text{-}Cl)_2(CO)_4$ regenerates **69** (Scheme 26).

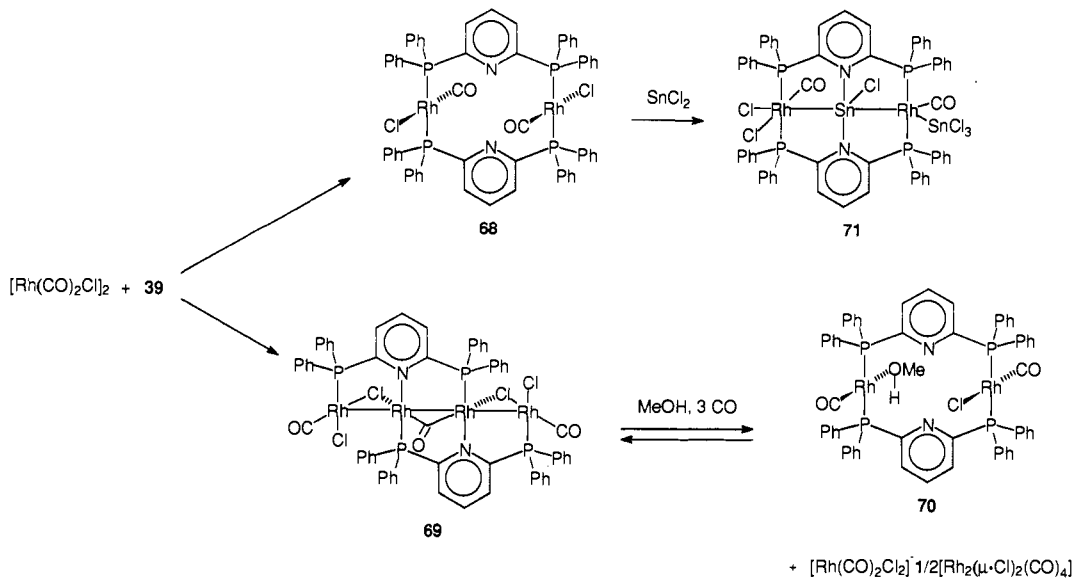
It is beyond the scope of this review to discuss the myriad of polynuclear metal pyridylphosphines; however, relevant data for most of the known complexes that have been thoroughly characterized are summarized in Tables 3–8. Tables 3–7 present the key ^{31}P NMR results, as well as other pertinent data 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 $RhCl[\mathbf{5}]_2$, $\{Rh(C_6H_{12})[\mathbf{5}]_2\}[PF_6]$, or $RhHCl[\mathbf{5}]_3$ was unsuccessful, when excess **5** and low CO and hydrogen (1:1) pressures were used with $RhH(CO)[P(C_6H_5)_3][\mathbf{5}]_2$, as catalyst

Scheme 26



+ $[Rh(CO)_2Cl_2]^-1/2[Rh_2(\mu\text{-}Cl)_2(CO)_4]$

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

palladium complexes	solvent/temp (K)	δ (ppm)	^3J (Hz)	ref(s)
$Pd(t\text{-BuNC})(3)Cl_2$	$CDCl_3$	24.5		107
$Pd(CH_2CMeCH_2)(3)Cl$	$CDCl_3$/255	24.3		107
cis-$Pd(pyrH)(4)Cl_2$	DMSO-d_6	30.5		69
cis,cis,trans-$Pd_3\{\mu\text{-}[(C_6H_5)_2P]_2pyr\}_3Br_6$		36.4, 19.9, 14.7		77
cis,cis,trans-$Pd_3\{\mu\text{-}[(C_6H_5)_2P]_2pyr\}_3Cl_6$	CD_2Cl_2	37.8, 23.0, 17.1		108, 77
trans-$Pd(3)_2Cl_2$	CD_2Cl_2	23.8, 23.4		22, 109, 110
	$CDCl_3$	22.9		111
cis-$Pd(3)_2Cl_2$	CD_2Cl_2	29.3, 29.5		22, 109, 110
	$CDCl_3$	28.5		111
2-pyr$(CH_2)_2P(C_6H_5)PdMeCN[BF_4]_2$	CD_3CN	47.0		75
cis-$PdCl_2(5)_2$	CD_2Cl_2/203	34.6		111
cis-$PdBr_2(5)_2$	CD_2Cl_2/203	32.1		111
trans-$PdI_2(5)_2$	CD_2Cl_2/203	7.0		111
cis-$PdCl_2(4)_2$	CD_2Cl_2	30.9		111
	$CDCl_3$	29.4		69
trans-$PdCl_2(4)_2$	CD_2Cl_2	17.7		111
	$CDCl_3$/203	17.7		69
cis-$PdBr_2(4)_2$	CD_2Cl_2/203	27.9		111
trans-$PdI_2(4)_2$	CD_2Cl_2/203	8.9		111
cis-$PdBr_2(3)_2$	CD_2Cl_2/203	20.5		111
trans-$PdI_2(3)_2$	CD_2Cl_2/203	9.6		111
$PdCl_2(5)_2$	CD_2Cl_2	6.3		111
$PdBr_2(5)_2$	CD_2Cl_2	4.35		111
$PdI_2(5)_2$	CD_2Cl_2	0.55		111
$Pd_2Cl_2(4)_2$	$CDCl_3$	5.2		111
$Pd_2Br_2(4)_2$	$CDCl_3$	3.28		111
$Pd_2I_2(4)_2$	$CDCl_3$	−0.16		111
$Pd_2Cl_2(3)_2$	CD_2Cl_2	4.4		22
	$CDCl_3$	4.4		111
$Pd_2Br_2(3)_2$	$CDCl_3$	2.92		111
$Pd_2I_2(3)_2$	CD_2Cl_2	−0.44		111
$Pd_2Cl_2(5)_2(\mu\text{-DMAD})$	$CDCl_3$	34.1		111
$Pd_2Cl_2(4)_2(\mu\text{-DMAD})$	$CDCl_3$	35.5, 35.3, 33.8, 33.3		111
$Pd_2Cl_2(3)_2(\mu\text{-DMAD})$	$CDCl_3$	35.8		111
$Pd_2(H_2O)_2(5)_2[BF_4]$	CD_3CN	−21.8		111
	D_2O	−19.8		111
$Pd_2(H_2O)_2(5)_2[PF_6]$	CD_3CN	−22.2		111
$Pd_2(H_2O)_2(5)_2[B(C_6H_5)_4]_2$	CD_3COCD_3	−22.6		111
$Pd(3)_2Cl[PF_6]$	$CDCl_3$	42.7, −42.3		110
$PdMo(\mu\text{-}3)_2(\mu\text{-CO})(CO)_2Cl_2$	$CDCl_3$	21.67, 31.09	(9.7)	112
$[t\text{-buNC})_2Cl_2Rh(\mu\text{-}3)Pd(\mu\text{-Cl}]_2$	$CDCl_3$	10.3, 11.1		107
$RhPd(\mu\text{-}3)_2(CO)Cl_3$	CD_2Cl_2	21.9, 16.1	113 (17.4) 2.3 ($^2J_{RhP}$)	113, 121
$RhPd(\mu\text{-}3)_2(CO)Br_3$	$CDCl_3$	19.6, 14.3	112.0 (17.3)	107
$RhPd(\mu\text{-}3)_2(MeNC)_2Cl_2[PF_6]$	$CDCl_3$	26.9, 17.5	108.9 (17.7)	107
$RhPd(\mu\text{-}3)_2(MeNC)_2Cl_2[B(C_6H_5)_4]$	$CDCl_3$	7.9	94.2	107
$RhPd(\mu\text{-}3)_2(MeNC)_2Cl_2[B(C_6H_5)_4]$	$CDCl_3$	27.6	109.3 (17.1)	107
$Pd\{[(C_6H_5)_2P]_2pyr\}_2Cl_2$		28.0, −1.6		77
$\{Pd\{[(C_6H_5)_2P]_2pyr\}_2Br_2\}_n$		18.1		77
HT-$[Pd_2Cl_2(\mu\text{-}Me_2Ppyr)_2]$		−23.56		114
HT-$[Pd_2Br_2(\mu\text{-}Me_2Ppyr)_2]$		−25.83		114
HT-$[Pd_2I_2(\mu\text{-}Me_2Ppyr)_2]$		−30.17		114
HH-$[Pd_2Cl_2(\mu\text{-}Me_2Ppyr)_2]^a$		−33.17		114
HH-$[Pd_2Br_2(\mu\text{-}Me_2Ppyr)_2]^a$		−36.29		114
HH-$[Pd_2Br_2(\mu\text{-}Me_2Ppyr)_2]^a$		−41.73		114
HT-$[PdPtCl_2(\mu\text{-}Me_2Ppyr)_2]$		−20.98	3910 ($^1J_{PPt}$)	114
HT-$[PdPtBr_2(\mu\text{-}Me_2Ppyr)_2]$		−22.88	3849 ($^1J_{PPt}$)	114
HT-$[PdPtI_2(\mu\text{-}Me_2Ppyr)_2]$		−26.79	3764 ($^1J_{PPt}$)	114
HT-$[Pd_2Cl_2(\mu\text{-}3)_2]$		−3.72		114
HT-$[Pd_2Br_2(\mu\text{-}3)_2]$		2.31		114
HT-$[Pd_2I_2(\mu\text{-}3)_2]$		0.37		114
HH-$[Pd_2Cl_2(\mu\text{-}3)_2]^a$		−12.38		114
HH-$[Pd_2Br_2(\mu\text{-}3)_2]^a$		−14.31		114
HH-$[Pd_2I_2(\mu\text{-}3)_2]^a$		−16.6		114
HT-$[PdPtCl_2(\mu\text{-}3)_2]$		7.06, −7.52	4049 ($^1J_{PPt}$)	114
	$CDCl_3$	7.4, −6.7	4048 ($^1J_{PPt}$)	117
HT-$[PdPtBr_2(\mu\text{-}3)_2]$		5.89, −8.89	3978 ($^1J_{PPt}$)	114
HH-$[PdPtI_2(\mu\text{-}3)_2]$	$CDCl_3$	−0.06	3213 ($^1J_{PPt}$)	117
HT-$[PdPtI_2(\mu\text{-}3)_2]$		3.46, −10.93	3894 ($^1J_{PPt}$)	114
	$CDCl_3$	3.9, −10.5	3891 ($^1J_{PPt}$)	117
$Rh(\eta^5\text{-}C_5H_5)(t\text{-BuNC})Pd(\mu\text{-}3)(t\text{-BuNC})Cl[PF_6]$	$CDCl_3$	37.19	148.4 ($^1J_{PRh}$)	115
$Rh(\eta^5\text{-}C_5H_5)(t\text{-BuNC})Pd(\mu\text{-}3)(t\text{-BuNC})Cl[Cl]$	$CDCl_3$	37.19	148.4 ($^1J_{PRh}$)	115
$(\eta\text{-}C_5H_5)Rh(CO)(\mu\text{-}3)PdCl_2$	$CDCl_3$	38.92	158.7 ($^1J_{PRh}$)	115
$PdRu(3)_2(CO)_2Cl_2$	CD_2Cl_2	38.9, 17.9		22
$PdRu(3)_2(CO_2)_2Cl_2$	CD_2Cl_2	20.1, 16.5		22
$Mo_2[2\text{-}(C_6H_5)_2Ppyr(6\text{-}O^-)]\cdot PdCl_2$	$CDCl_3$	16		116
$Mo_2[2\text{-}(C_6H_5)_2Ppyr(6\text{-}O^-)]\cdot PdBr_2$	$CDCl_3$	16		116
$PdCl_2[2\text{-}(C_6H_5)_2Ppyr(6\text{-}O^-)]_2$	$CDCl_3$	17		116
$[PdCl(NIPHOSH\cdot OH)(PMe_3)][PdCl_3(PMe_3)]^b$	CD_3CN	75.5		79
$[PdCl(NIPHOSH\cdot OMe)(PMe_3)][SbF_6]^b$	CD_3CN	107.7		79
$[PdCl(NIPHOS)(PMe_3)]PdCl_3(PMe_3)]^b$	$CDCl_3$	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

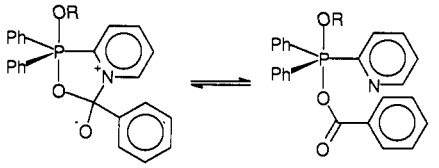
platinum complexes	solvent/temp (K)	δ (ppm)	^1J (Pt–P) [$^2J_{PP}$]	ref(s)
$Pt(5)_4$	$CDCl_3$/228	30.1	3829	76
		−538.3 [δ Pt]	3840	
$Pt(3)_3$	toluene-d_8	57.02	4444	76
	228	−300.3 [δ Pt]	4433	
trans-$Pt(H)Cl(3)_2$	CD_2Cl_2/298	30.00	3031	76
trans-$PtIMe(3)_2$	$CDCl_3$/298	26.82	3078	76
trans-$PtIMe(5)_2$	$CDCl_3$/298	25.64	3133	76
cis-$PtMe_2(3)_2$	$CDCl_3$	27.3	1875	71
trans-$PtMeCl(3)_2$	$CDCl_3$	22.0	3157	71
trans-$PtMeI(3)_2$	$CDCl_3$	25.9	3091 [12]	71
$PtMe(\eta^2\text{-}3)(3)[B(C_6H_5)_4]$	$CDCl_3$	−17.6	1391 [12]	71
		19.2	4226 [12]	
trans-$PtMe(SnCl_3)(3)_2$		61.7	3060	71
			217 ($^2J_{SnP}$)	
cis-$Pt(3)_2I_2$	$CDCl_3$	6.7	3514	70, 117
		11.9	3453	118
trans-$Pt(3)_2I_2$	$CDCl_3$	9.8	2503	70, 117, 118
$[Pt(3)_2I]I$	$CDCl_3$	19.3	3637	117, 118
		−61.2	3241	
$Pt(3)_2(\eta^2\text{-}CH_2{=}CHCN)$	$CDCl_3$/298	30.7	3445 [34.7]	76
		31.7	3969	
$Pt(5)_2(\eta^2\text{-}CH_2{=}CHCN)$	$CDCl_3$/228	34.6	3406 [31.9]	76
		35.4	3934	
$Pt(3)_2(\eta^2\text{-}CH_2{=}CMeCN)$	$CDCl_3$/298	31.3	3538 [35.2]	76
		31.3	3718	
$Pt(3)_2(\eta^2\text{-}CHMe{=}CHCN)$	$CDCl_3$/298	31.8	3265 [38.5]	76
		32.6	4095	
$Pt(3)_2(\eta^2\text{-}CHMe{=}CHCN)$	$CDCl_3$/298	31.6	3240 [39.4]	76
		32.1	4086	
$Pt(3)_2(\eta^2\text{-}C_4H_2O_3)$	$CDCl_3$/298	27.0	3841	76
$Pt(3)_2[\eta^2\text{-}cis\text{-}(CHCO_2Et)_2]$	$CDCl_3$/298	30.0	3750	76
$Pt(3)_2[\eta^2\text{-}trans\text{-}(CHCO_2Et)_2]$	$CDCl_3$/298	28.1	3815	76
$\{Pt\{[(C_6H_5)_2P]_2pyr\}_2Cl_2\}_n$		14.3	3647	77
trans,trans-$Pt_2\{[\mu\text{-}(C_6H_5)_2P]_2pyr\}_2I_4$		6.2	2595	77
HT-$[Pt_2Cl_2(\mu\text{-}Me_2Ppyr)_2]$		−31.78	3985 [18.9]	114
			213 ($^2J_{PPt}$)	
HT-$[Pt_2Br_2(\mu\text{-}Me_2Ppyr)_2]$		−34.13	3919 [18.9]	114
			212.4 ($^2J_{PPt}$)	
HT-$[Pt_2I_2(\mu\text{-}Me_2Ppyr)_2]$		−38.00	3827 [18.9]	114
			199.1 ($^2J_{PPt}$)	
HH-$[Pt_2I_2(\mu\text{-}Me_2Ppyr)_2]^a$		−16.84	2957	114
			131.2 ($^2J_{PPt}$)	
HT-$[PtPdI_2(\mu\text{-}Me_2Ppyr)_2]$		−37.16	3910 [14.5]	114
			90.1 ($^2J_{PPt}$)	
HT-$[PtPdBr_2(\mu\text{-}Me_2Ppyr)_2]$		−39.34	3849 [15.6]	114
			71.2 ($^2J_{PPt}$)	
HT-$[PtPdI_2(\mu\text{-}Me_2Ppyr)_2]$		−42.96	3764 [16.7]	114
			37.8 ($^2J_{PPt}$)	
HH-$[PtPdI_2(\mu\text{-}Me_2Ppyr)_2]^a$		−27.08	2912	114
HT-$[Pt_2Cl_2(\mu\text{-}3)_2]$		−2.29	4128 [17.8]	114
	$CDCl_3$	−1.5	4124 [17.8]	117
HT-$[Pt_2Br_2(\mu\text{-}3)_2]$		−3.75	4048 [17.8]	114
			213.5 ($^2J_{PPt}$)	
HT-$[Pt_2I_2(\mu\text{-}3)_2]$		−6.25	3965 [20.0]	114
	$CDCl_3$	−5.7	3905 [17.7]	117
HH-$[Pt_2Cl_2(\mu\text{-}3)_2]$		14.64		114
	$CDCl_3$	9.6	3263	117
HH-$[Pt_2Br_2(\mu\text{-}3)_2]$		12.17	3589	114
			160.1 ($^2J_{PPt}$)	
HH-$[Pt_2I_2(\mu\text{-}3)_2]$		9.34	3263	114
	$CDCl_3$	9.6	3263	117
HT-$[PtPdCl_2(\mu\text{-}3)_2]$		−7.52	4049 [14.5]	114
	$CDCl_3$	−6.7	4048 [14.3]	117
HT-$[PtPdBr_2(\mu\text{-}3)_2]$		−8.89	3978 [15.6]	114
			91.2 ($^2J_{PPt}$)	
HH-$[PtPdI_2(\mu\text{-}3)_2]$	$CDCl_3$	−0.06	3213	117
HT-$[PtPdI_2(\mu\text{-}3)_2]$		−10.93	3894 [16.1]	114
	$CDCl_3$	−10.5	3891 [16.0]	117
cis-$Pt(3)_2Cl_2$	CD_2Cl_2	11.62	3675.6	113
	$CDCl_3$	11.6	3676	117, 118
$[Pt(3)_2Cl]Cl$	$CDCl_3$	15.2	3304	117, 118
		−50.03	3339	
$Pt(3)_2Br_2$	CD_2Cl_2	10.86	3618	113
$Pt(3\text{-}PO)Br_4$		25.4		82
$PtCl_2[pyr(CH_2)_2PH(C_6H_5)]$		33.64		74

Table 4 (Continued)

platinum complexes	solvent/temp (K)	δ (ppm)	^1J (Pt-P) [$^2J_{PP}$]	ref(s)
$PtMo(\mu\text{-}3)_2(\mu\text{-}CO)(CO)_2Cl_2$	$CDCl_3$	34.4	3064	119
$PtRh(3)_2(CO)Cl_3$	CD_2Cl_2	1.04	4035 [14.0] ≈133 ($^2J_{PPt}$)	113
$PtRh(3)_2(CO)Cl_5$	CD_2Cl_2	−17.9	2793.3 [19.7] 63.0 ($^2J_{PPt}$)	113
$PtRh(3)_2(CO)Br_3$	CD_2Cl_2	0.13	3950 [15]	113
$PtRh(3)_2(CO)Br_5$	CD_2Cl_2	−20.7	2776 [15] 368 ($^2J_{PPt}$)	113
$[Pt(3)_2Cl][Rh(CO)_2Cl_2]$	CD_2Cl_2	15.24	3704	113
$(\eta\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}3)Pt(Me)_2$	$CDCl_3$	50.0	125.6 ($^2J_{PPt}$)	115
$(\eta\text{-}C_5H_5)Rh(Cl)(\mu\text{-}3)Pt(CO)Cl$	$CDCl_3$	40.93	165.9 ($^2J_{PPt}$)	115
$[Pt(3)_2Cl][Rh(CO)_2Cl_2]$	$CDCl_3$	15.2, −50.3	3704, 3339	117
$[Pt(3)_2I][PF_6]$	$CDCl_3$	19.3, −61.2	3637, 3241	117
$PtRh[P(C_6H_5)_2](pyrCH[P(C_6H_5)_2]_2)$-$(pyrCH_2P(C_6H_5)_2)(P(C_6H_5)_3)[BF_4]_2$	CH_2Cl_2/163	157.2 29.4 27.62 19.62 17.55	129 (J_{RhP}) 130 3115 (J_{PtP}) 3457 (J_{PtP})	120
$[PtCl(NIPHOS)P(C_6H_5)_3][PtCl_3P(C_6H_5)_3]$[b]	$CDCl_3$	155.1	4526	79
$[PtCl(NIPHOS)(PMeC_6H_5)_2][PtCl_3(PMeC_6H_5)_2]$[b]	$CDCl_3$	155.0	4582	79
$[PtCl(NIPHOS)(PMe_2C_6H_5)][PtCl_3(PMe_2C_6H_5)]$[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
$[PtCl(NIPHOSH{\cdot}OH)(P(C_6H_5)_3)]^+$[b]	$CDCl_3$	50.9	3936	79
$[PtCl(NIPHOSH{\cdot}OH)(PMe(C_6H_5)_2)]^+$[b]	$CDCl_3$	53.5	3987	79
$[PtCl(NIPHOSH{\cdot}OH)(PMe_2C_6H_5)]^+$[b]	$CDCl_3$	52.8	4002	79
$[PtCl(NIPHOSH{\cdot}OH)(PMe_3)]^+$[b]	$CDCl_3$	54.7	4059	79
$[PtCl(NIPHOSH{\cdot}OH)(Pbu_3)]^+$[b]	$CDCl_3$	54.5	4152	79
$[PtCl(NIPHOSH{\cdot}OH)(AsMe_2C_6H_5)]^+$[b]	$CDCl_3$	55.0	3873	79
$[PtCl(NIPHOSH{\cdot}OMe)(PMe_3)]^+$[b]	CD_3CN	80.0	4156	79
[PtCl(NIPHOSH·O*i*-Pr)(PMe_3)]$^+$[b]	$CDCl_3$	72.0	4138	79
[PtCl(NIPHOSH·Oisoamyl)(PMe_3)]$^+$[b]	$CDCl_3$	75.4	4162	79
$[PtCl(NIPHOSH{\cdot}OC_6H_5)(PMe_3)]^+$[b]	$CDCl_3$	80.4	4296	79
$[PtCl(NIPHOSH{\cdot}SC_6H_5)(PMe_3)]^+$[b]	$CDCl_3$	28.6	3872	79

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

Scheme 27



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(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)$_2$-$P(C_6H_5)$,[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)-$(4\text{-}MeC_6H_4)P(C_4H_9)$ (98.9%).[171]

Several new pyridylphosphine catalysts $FeRh(3)_2(CO)_3Cl$, $NiRh(3)_2(CO)Cl_3$, and $CoRh(3)_2(CO)Cl_3$ have recently been prepared[72] from $Fe(3)_2(CO)_2(CS_2)$, $Ni(3)_2(CO)_2$, and $CoRh(3)_2Cl_2$, 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 $(C_6H_{11})P[(CH_2)_2(2\text{-pyr})]$ and $Ni(COD)_2$ under CO_2 (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 hydroformylated[78] using a water-soluble catalyst consisting of $Rh_4(CO)_{12}$ 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 $(\eta^5\text{-}C_5H_5)Rh_2(\mu\text{-}CO)(\mu\text{-}3)$-(CO)Cl as a hydroformylation catalyst; the formation of the intermediates was followed by ^{31}P NMR spectra.

2. Chlorinations

When primary or secondary alkyl alcohols were treated with $2\text{-pyr}(CH_2)_2P(C_6H_5)_2$ in $CCl_4/CHCl_3$ at 35–45 °C, high yields of the corresponding alkyl chloride were obtained.[45] The reaction complexes were studied by ^{31}P 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)	$^1J_{RhP}$ [$^2J_{PP}$]	ref(s)
$Rh(3)_2(CO)Cl$	$CDCl_3$	30.13	127.8	110, 121
$Rh(3)_2(CO)Br$	$CDCl_3$	29.1	125.9	110
$Rh(MeNC)_2(3)_2[PF_6]$	$CDCl_3$/233	28.3	130.5	110
$Rh(MeNC)_2(3)_2[B(C_6H_5)_4]$	$CDCl_3$/233	28.3	128.5	110
$RhPd(\mu\text{-}3)_2(CO)Cl_3$	CD_2Cl_2	21.9, 16.1	112.7 [17.4] 2.3 ($^2J_{RhP}$)	110, 113, 121
$RhPd(\mu\text{-}3)_2(CO)Br_3$	$CDCl_3$	19.6, 14.3	112.0 [17.3]	110
$RhPd(\mu\text{-}3)_2(MeNC)_2Cl_2[PF_6]$	$CDCl_3$	26.9, 17.5	108.9 [17.7]	110
$RhPd(\mu\text{-}3)_2(MeNC)_2Cl_2[B(C_6H_5)_4]$	$CDCl_3$	7.9	94.2	110
$RhPd(\mu\text{-}3)_2(MeNC)_2Cl_2[B(C_6H_5)_4]$	$CDCl_3$	27.6	109.3 [17.1]	110
$Rh[P(C_6H_5)_3](CO)(3)Cl$	toluene-d_8	27.8	128	107
$Rh[P(C_6H_5)_3]_2(3)(CO)(Cl)$	215	41.0	140.8 [22]	172
		45.8	154.8 [22]	
$Rh[P(C_6H_5)_3](3)_2(CO)(Cl)$	215	42.2	154.5 [37.8]	172
		45.9	155.1 [37.8]	
$[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-DMA})(\mu\text{-}3)Rh(CO)\mu\text{-}Cl]_2$	CD_2Cl_2/298	53.4	175.9 [4.8]	145
	225	54.1	175.6 [4.8]	
		55.3	174.9 [4.6]	
$[(\eta^5\text{-}C_5H_5)Rh(\mu\text{-DMA})(\mu\text{-}3)Rh(CO)(SO_2)Cl]$	CD_2Cl_2	60.9	162 [3.7]	145
$Rh(C_8H_{12})(3)Cl$	$CDCl_3$	29.7, 30.6	150.2, 150.3	122
	CD_2Cl_2	29.3	150.1	107
$Rh(acac)(Cl)CH_2[Ppyr(C_6H_5)]_2CH_2[Cl]$		63.7, 90.0	122, 139 [15]	147
		62.9, 93.7	123, 135 [14]	
$Rh(acac)(Cl)CH_2[Ppyr(C_6H_5)]_2(CH_2)_3[Cl]$		22.8, 60.9	116, 130 [36]	147
		20.4, 60.2	116, 131 [37]	
		23.3, 61.0	116, 125 [50]	
		22.9, 60.7	118, 125 [51]	
$Rh(dpm)(Cl)CH_2[Ppyr(C_6H_5)]_2(CH_2)_2[Cl]$		62.9, 88.1	121, 140 [16]	147
		62.4, 91.2	122, 136 [14]	
$Rh(dpm)(Cl)CH_2[Ppyr(C_6H_5)]_2(CH_2)_3[Cl]$		20.8, 59.9	116, 131 [38]	147
		19.5, 58.6	115, 131 [38]	
$Rh(dpm)(Cl)CH_2[pyrPMe_2][Cl]$		23.8, 54.0	125, 131 [46]	147
$Rh(acac)(Cl)(CH_2Cl)[Ppyr(C_6H_5)]_2CH_2$		−18.8, −11.0	118, 124 [84]	147
		−12.9	117	
$Rh(acac)(Cl)(CH_2Cl)[Ppyr(C_6H_5)]_2(CH_2)_2$		58.6, 61.8	137, 147 [17]	147
		51.5	137	
$Rh(acac)(Cl)(CH_2Cl)[Ppyr(C_6H_5)]_2(CH_2)_3$		19.0, 22.2	126, 134 [40]	147
		24.2	127	
$Rh(dpm)(Cl)(CH_2Cl)[Ppyr(C_6H_5)]_2CH_2$		−17.5, −11.6	117, 126 [85]	147
		−11.7	117	
$Rh(dpm)(Cl)(CH_2Cl)[Ppyr(C_6H_5)]_2(CH_2)_2$		55.2, 59.2	136, 148 [19]	147
		53.4	137	
$Rh(dpm)(Cl)(CH_2Cl)[Ppyr(C_6H_5)]_2(CH_2)_3$		18.1, 20.7	126, 138 [40]	147
		24.3	129	
$Rh(dpm)[Ppyr(C_6H_5)_2]_2CH_2$		−16.2	159	147
$Rh(dpm)[Ppyr(C_6H_5)_2]_2(CH_2)_2$		75.2	189 [48]	147
$Rh(dpm)[Ppyr(C_6H_5)_2]_2(CH_2)_3$		39.9	178 [75]	147
$Rh(dpm)(pyrPMe_2)$		27.7	186	147
$Rh(acac)[Ppyr(C_6H_5)_2]_2(CH_2)_2$		73.8	188 [49]	147
$Rh(acac)[Ppyr(C_6H_5)_2]_2(CH_2)_3$		38.9	178 [73]	147
$Rh_2(form)_2(\mu\text{-}O_2CCF_3)(\mu\text{-}3)(O_2CCF_3)$	$CDCl_3$/225	−34.36	82.8 [55.4]	142
	310	30.21	127.0 [5.7]	
		29.53	126.4 [5.3]	
	CD_3CN/310	30.9	127.6 [3.3]	
$Rh(form)_2(\mu\text{-}3)_2(O_2CCF_3)_2$	$CDCl_3$/225	−96.05		142
	$CDCl_3$/310	29.01	132	
	CD_3CN/310	25.83	129.7	
$[Rh_2(form)_2(\mu\text{-}3)(\mu\text{-}O_2CCF_3)][PF_6)$	$CDCl_3$/310	29.68	122.2 [5.2]	142
$Rh_2(form)_2(\mu\text{-}3)(O_2CCF_3)[PF_6]$	$CDCl_3$/310	26.8	127.1	142
$Rh_2(form)_2(\mu\text{-}3)_2[(PF_6)_2]$	$CDCl_3$/310	28.74	131.1	142
$Rh_2(form)_2(\mu\text{-}3)(\mu\text{-}O_2CCF_3)[Cl]$	$CDCl_3$/225	24.35	164.5 [5.8]	142
$Rh_2(form)_2(\mu\text{-}3)(\mu\text{-}O_2CCF_3)[Br]$	$CDCl_3$/310	28.79	122.2 [5.4]	142
$Rh_2(form)_2(\mu\text{-}3)_2(\mu\text{-}O_2CCF_3)[Cl]$	$CDCl_3$/310	27.90	131.3	142
$Rh_2(form)_2(\mu\text{-}3)_2I_2$	$DCCl_3$/310	27.82	129.9	142
$Rh(\eta^5\text{-}C_5H_5)(CO)(3)$	$CDCl_3$	53.80	199.8	143
$(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}CO)(\mu\text{-}3)Rh(CO)Cl$	$CDCl_3$	52.10	175.6 [5.3]	143
$(\eta^5\text{-}C_5H_5)Rh(\mu\text{-}3)(\mu\text{-}SO_2)Rh(CO)Cl$	$CDCl_3$	60.3	162.2 [3.8]	143
$[(t\text{-buNC})_2Cl_2Rh(\mu\text{-}3)Pd(\mu\text{-}Cl)]_2$	$CDCl_3$	10.3, 11.1		107
$Rh(acac)[Ppyr(C_6H_5)]_2CH_2$		−19.2	164	147
$Rh(acac)[Ppyr(C_6H_5)]_2(CH_2)_2$		70.0	194 [51]	147
$Rh(acac)[Ppyr(C_6H_5)]_2(CH_2)_3$		37.3	182	147
$Rh(dpm)[Ppyr(C_6H_5)]_2CH_2$		−18.5	164	147
$Rh(dpm)[Ppyr(C_6H_5)]_2(CH_2)_2$		72.1	194 [52]	147
$Rh_2Sn_2(CO)_2Cl_6[\mu\text{-}2,6\text{-}pyr(P(C_6H_5)_2)_2]_2$	C_6D_6/298	42.2	91.8	149
		67.1	141.0	

Table 5 (Continued)

rhodium complexes	solvent/temp (K)	δ (ppm)	$^1J_{RhP}$ [$^2J_{PP}$]	ref(s)
$Rh_2(CO)_2Cl_2[\mu$-2,6-pyr$(P(C_6H_5)_2)_2]_2$	$CDCl_3$/293	28.6	132	149
		29.3	124	
		30.0	127	
$Rh_4[2,6$-pyr$(P(C_6H_5)_2)_2]_2(\mu$-CO$)(CO)_2(\mu$-Cl$)_2Cl_3$		39.9	129.7	108, 149
		36.2	149.7	
$Rh_4[\mu$-2,6-pyr$(P(C_6H_5)_2)_2]_2(\mu$-$SO_2)(CO)_2Cl_4$		35.7	131	150
		30.7	138	
$[Rh_2(CO)[\mu$-2,6-pyr$(P(C_6H_5)_2)_2]_2(CH_3OH)Cl]^+$		31.1	128.2	150
		20.4	128.9	
rac-$[(C_6H_5)$pyrP$]_2(CH_2)[Rh(CO)Cl_2]_2$	DMSO-d_6	36.9	161 [67]	19
{*meso*-$[(C_6H_5)$pyrP$]_2(CH_2)_2Rh_2Cl_2\}[Rh(CO)Cl_2]_2$	CD_3OD–CD_3CN	24.0	≈112	19
$[Rh_2\{\mu$-$[(C_6H_5)_2P]$pyr$\}_2(\mu$-CO$)(\mu$-I$)][B(C_6H_5)_4]$	$CDCl_3$/298	61.3	153	123
		−41.3	135	
$\{(C_6H_{12})Rh[(C_6H_5)_2Ppyr]_2\}_2$	CD_2Cl_2	25.1	144	73
$\{(CO)_2Rh[(C_6H_5)_2P$pyr$]_2\}_2[BF_4]$	CD_2Cl_2/183	40.5	75	73
$RhPt(3)_2(CO)Cl_3$	CD_2Cl_2	24.6	114 [2.9]	113
$RhPt(3)_2(CO)Cl_5$	CD_2Cl_2	27.9	110	113
$RhPt(3)_2(CO)Br_3$	CD_2Cl_2	24.0	110	113
$RhPt(3)_2(CO)Br_5$	CD_2Cl_2	27.6	112	113
$Rh_2(3)_2(\mu$-CO$)Cl_2$	CD_2Cl_2	44.18	144.0 [16.0]	121, 124
			12.0 (J_{RhRh})	
			−7.39 ($^2J_{RhP}$)	
$(\eta^5$-$C_6H_5)(t$-buNC$)Rh(\mu$-3$)Pd(t$-buNC$)(Cl)[PF_6]$	$CDCl_3$	37.19	148.4	115
$(\eta^5$-$C_6H_5)(t$-buNC$)Rh(\mu$-3$)Pd(t$-buNC$)(Cl)[Cl]$	$CDCl_3$	37.19	148.4	115
$(\eta^5$-$C_6H_5)(CO)Rh(\mu$-3$)PdCl_2$	$CDCl_3$	38.92	158.7	115
$(\eta^5$-$C_6H_5)(\mu$-CO$)Rh(\mu$-3$)PtMe_2$	$CDCl_3$	50.0	190.2	115
			125.6 ($^2J_{PPt}$)	
$(\eta^5$-$C_5H_5)(Cl)Rh(\mu$-3$)Pt(CO)Cl$	$CDCl_3$	40.93	152.48	115
			165.9 ($^2J_{PPt}$)	
$Rh_2(\mu$-3$)_2(\mu$-Cl$)(CO)Cl_3$	248	29.7	117.2	125
		23.2	109.9	
$Rh_2(\mu$-3$)_2(CO)Cl_4$	$(ClCH_2)_2$/348	27.6	≈124.5	125
$Rh_2(\mu$-3$)_2(CO)_2Cl_4$		22.4	109.9	125
$Rh_2(\mu$-3$)_2(t$-buNC$)_2Cl_4$		25.3	113.0	125
$Rh_2(3)(\mu$-$SO_2)Cl_2$		41.70	138.4 [18]	124
			−6.2 ($^2J_{PRh}$)	
$Rh_2(CO)[\mu$-pyrCH$(P(C_6H_5)_2)_2]_2[B(C_6H_5)_4]_2$	acetone, 293	61.5	136, 130 (J_d)	126
		37.7	30.5, 30.5 (J_t)	
$PtRh[P(C_6H_5)_2](pyrCH[P(C_6H_5)_2]_2)(pyrCH_2$-$P(C_6H_5)_2)(P(C_6H_5)_3)[BF_4]_2$	CH_2Cl_2/163	157.2	5129 (J_{RhP})	127
		29.4	130	
		27.62	3115 (J_{PtP})	
		19.62		
		17.5	3457 (J_{PtP})	
$Rh[pyrCH(P(C_6H_5)_2]_2[BF_4]$	CH_2Cl_2	1.06	115.6 (J_{RhP})	128
$RhAg[pyrCH(P(C_6H_5)_2][BF_4][NO_3]$	CH_2Cl_2	53.84	143 (J_{RhP})[50,37]	127
		25.66	543, 468 (J_{AgP})[50,37]	
$RhAg[pyrCH(P(C_6H_5)_2](CO)_2[BF_4NO_3]$	CH_2Cl_2	51.99	140	127
		49.93		
$RhAu[pyrCH(P(C_6H_5)_2]Cl[BF_4]$	CH_2Cl_2	68.89	171	127
		42.82		
$RhAu[pyrCH(P(C_6H_5)_2)_2Br[BF_4]$	CH_2Cl_2	68.34	170	127
		43.33		
$RhAu[pyrCH(P(C_6H_5)_2)_2[BF_4NO_3]$	CH_2Cl_2	76.02	~162	128
$\{Rh_2[pyrCH(P(C_6H_5)_2)]_2(CO)_2\}[PF_6]\cdot C_3H_6O$	MeCOMe	62.0	117.9 (J_{RhP});	129
			293.5, 54.1 (J_{PP})	
		40.2	134.5 (J_{RhP});	
			293.0, 54.0 (J_{PP})	
$Rh(CO)(Cl)[pyrCH(P(C_6H_5)_2)]_2$	MeCOMe	69.1	168 (J_{RhP})[107]	129
		0.35	[108]	
$Rh(\mu$-S$)(CO)_2[pyrCH(P(C_6H_5)_2)]_2$	$CDCl_3$	34.1	139	129
$Rh(CO)ZnCl(\mu$-Cl$)\{2,6$-pyr$[CH_2O(CH_2)_3P(C_6H_5)_2]_2\}(CF_3SO_3)$	CH_2Cl_2	26.4	119	46
$[Rh_2(NBD)_2(NIPHOS)_2][SbF_6]_2$	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 = acetylacetone. Form = di-*p*-tolylformamidinate.

P-oxide by a previously reported $CeCl_3/LiAlH_4$ procedure.[173] The mechanism of this esterification has been further studied[174] using ^{31}P NMR, revealing the presence of a dialkoxyphosphorane intermediate in equilibrium with the alkoxyphosphonium carboxylate species; details were presented.

Camp and Jenkins[174] have used **3** in the Mitsunobu reaction to circumvent the difficulties associated with the use of triphenylphospine oxide.[175] They suggested[174] 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 Molybdium Pyridylphosphine Complexes

molybdium complexes	solvent	δ (ppm)	$^1J_{PH}$	ref
cis-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_2Cl_2	−83.1	339	29
(2-pyrPH$_2$)$_2$Mo(CO)$_4$	CD_2Cl_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_6D_6	−81.8	322	36
2-pyrCH$_2$PH$_2$Mo(CO)$_4$	CD_2Cl_2	−1.4	345	36
2-pyr(CH$_2$)$_2$PH(C$_6$H$_5$)Mo(CO)$_4$	CD_2Cl_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_2Cl_2	−61.8, −74.7	22 ($^2J_{PP}$)	36
2-pyr(CH$_2$)$_2$PH$_2$Mo(CO)$_5$	C_6D_6	−80.8	318	36
2-pyrCH$_2$PH(C$_6$H$_5$)Mo(CO)$_5$	CD_2Cl_2	−4.4	339	36
2-pyr(CH$_2$)$_2$PH$_2$[Mo(CO)$_2$(η^5-C$_5$H$_5$)]$_2$	CD_2CL_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_2Cl_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 ($^1J_{PW}$)	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$_6$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_{PtP})	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 determined[175] and compared to the corresponding triphenylphosphine betaines.

4. Epoxidation of Alkenes

It has been reported[176] that ruthenium(II) complexes, specifically RuCl[(C$_6$H$_5$)$_2$P(CH$_2$)$_2$(2-pyr)]$_2$[ClO$_4$], promote the oxidation of several alkenes by C$_6$H$_5$IO, hypochlorates, and hydrogen peroxide. Typically, the reaction of alkene (0.1 M), catalyst (2 mM), and C$_6$H$_5$-IO in CH_2Cl_2 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 CO_2 and diynes has been reported.[56,57] The use of (2-pyr)(CH$_2$)$_2$P(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 Minato[177] reported the easy Pd-catalyzed dimerization of isoprene, using Pd(acac)$_2$, (C$_6$H$_{11}$)-P[(CH$_2$)$_2$(2-pyr)]$_2$, and DBU under CO_2 pressure in the presence of tri-*n*-butyltin ethoxide. A mixture of two "C$_{10}$H$_{15}$CO$_2$CH$_3$" 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 reported[135] using cyclooctene.

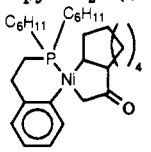
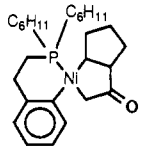
IV. Conclusions

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 structures[10] in view of Vögtle's superstructures[178] 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 Jenkins[174] in their studies of the Mitsunobu reaction.

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

complexes	solvent/temp (K)	δ (ppm)	$^1J_{PH}$	ref(s)
$(\eta^5\text{-}C_5H_4)Co_2(CH_3)Co(3)I_2$	$CDCl_3$	35.8		133
2-pyr$PH_2Ni(CO)_3$	CD_2Cl_2	−71.1	313	29
$Re_2(CO)_8[\eta^2,\eta^2\text{-pyrCH}(P(C_6H_5)_2)_2]$	CD_2Cl_2	21.3		148
$Re_2(CO)_7[\mu\text{-}\eta^1,\eta^4\text{-pyrCH-}(P(C_6H_5)_2)_2][\mu\text{-}P(C_6H_5)_2]$	$CDCl_3$/253	70.3 −12.8	24 (J_{PP}) 22 (J_{PP})	148
$Re_2Cl_4(3)_3$	$CDCl_3$–CH_2Cl_2 (1:1)	−6.150, −5.45, −0.37	11.1 ($^2J_{PP}$), 6.7, 4.9 ($^3J_{PP}$)	23
$Re_2Cl_3(3)_2[(C_6H_5)(C_6H_4)Ppyr]$	$CDCl_3$–CH_2Cl_2 (1:1)	−25.81, −0.88, 14.66	16.3 ($^2J_{PP}$), 9.3, 6.9 ($^3J_{PP}$)	23, 134
$Re_2Cl_2(3)_4[PF_6]$	$CDCl_3$–CH_2Cl_2 (1:1)	11.76		23
$Re_2Cl_4(3)_2(PEt_3)$	$CDCl_3$–CH_2Cl_2 (1:1)	−25.48, −7.24, 13.68		23
$ReCl_4(3)_2(Pbu_3)$	$CDCl_3$–CH_2Cl_2 (1:1)	−29.71, −8.31, 13.73	10.0 ($^2J_{PP}$), 7.0, 3.9 ($^3J_{PP}$)	23
2-pyr$PH_2W(CO)_5$	CD_2Cl_2	−89.9	343	29
	DMF-d_7	36.1		135
	CD_2Cl_2	38.3		136
$Ru_3(\mu\text{-}\eta^2C(O)C_6H_5)(\mu_3\text{-}\eta^2\text{-Ppyr}(C_6H_5)(CO)_9$	$CDCl_3$	48.93		146
$Ru_3(\mu\text{-}\eta^2C(O)C_6H_5)(\mu_3\text{-}\eta^2\text{-Ppyr}(C_6H_5)\text{-}(CO)_8[P(C_6H_5)_3]$	$CDCl_3$	49.53, 26.26	17.60 (J_{PP})	146
$Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-Ppyr}(C_6H_5)(CO)_9$	$CDCl_3$	118.05		146
2,6-$[(C_6H_5)_2P]_2$pyr$[Cr(CO)_5]_2$		57.5		25
2,6-$[(C_6H_5)_2PO]$pyr$[P(C_6H_5)_2Cr(CO)_5]$		58.3, 19.3	2.4 (J_{PP})	25
2,6-$[(C_6H_5)_2P]$pyr$[W(CO)_5]_2$		23.1	239 ($^1J_{PW}$)	25
2,6-$[(C_6H_5)_2P]$pyr$[W(CO)_5]$		21.7, −3.3		25
$Cu_2(\mu\text{-}3)_2(MeCN)_2[BF_4]_2$	CD_2Cl_2/295	7.44, 4.68		137
$Cu_2(\mu\text{-}3)_2(MeCN)_4[BF_4]_2$	CD_2Cl_2/295	7.69, 4.77		137
$Cu_2(\mu\text{-}3)_3[BF_4]_2$	CD_2Cl_2/295	4.63		137
$Cu_2(\mu\text{-}3)_3(MeCN)[BF_4]_2$	CD_2Cl_2/295	5.45		137
$Cu_2(\mu\text{-}3)_3[P(OMe)_3]_2[BF_4]_2$	$CDCl_3$/293	1.70		137
$Cu_2(\mu\text{-}3)_3(PMe_3)_2[BF_4]_2$	$CDCl_3$/293	1.46, −43.11		137
$Cu_2(\mu\text{-}3)_3$(4-Mepyr)$_2[BF_4]_2$	$CDCl_3$/293	1.82		137
$Cu_2(\mu\text{-}3)_3$(2-Mepyr)$[BF_4]_2$	$CDCl_3$/293	4.79		137
$Cr(CO)_5(3)$	$CDCl_3$	59.37		131
$W(CO)_5(3)$	$CDCl_3$	24.36	122.07 (J_{PW})	131
$Cr(CO)_4(3)_2$	$CDCl_3$	75.52		131
$W(CO)_4(3)_2$	$CDCl_3$	25.03		131
$UO_2(NO_3)_2[(C_6H_5)_2PO]$pyrO	$CDCl_3$/300	31.1		86
$Ru_3(CO)_9(3)_3$	CD_2Cl_2	37.7		22
$Ru_3(3)_2(CO)_3$	CD_2Cl_2	57.8		22
$Ru(3)(CO_2)Cl_2$	CD_2Cl_2	−6.8		22, 70
$Ru(3)(CO)_2Cl_2$	CD_2Cl_2	21.5		22
$RuPd(3)_2(CO)Cl_2$	CD_2Cl_2	38.9, 17.9, 20.1, 16.5		22
$Ru(3)(CO)_2Br_2$	CD_2Cl_2	−8.87		70
$Ru(3)_2(CO_2)Cl_2$	CD_2Cl_2	21.49		70
Au(2-pyrPMe_2)Cl	$CDCl_3$	−5.95		18
Au$[(2\text{-pyr})_2PMe]Cl$	$CDCl_3$	19.60		18
Au$[(2\text{-pyr})_3P]Cl$	$CDCl_3$	32.24		18
Au$[(2\text{-pyr})P(C_6H_5)_2]Cl$	$CDCl_3$	32.66		18
Au$[(2\text{-pyr})_2P(C_6H_5)]Cl$	$CDCl_3$	32.41		18
$RuH(Cl)(5)_3$	CD_2Cl_2	74.7		8
$Ru(Cl)_2(5)_2$	CD_2Cl_2	−0.3		8
$[Ir_2(COD)_2(NIPHOS)_2][SbF_6]$[a]	CD_3CN	108.0		130
$[Ir_2(NBD)_2(NIPHOS)_2][SbF_6]$[a]	$(CD_3)_2CO$	107.9		130
$Ir(C_6H_{12})[pyrCH(P(C_6H_5)_2)_2][BF_4]$	CH_2Cl_2	9.6		129
$Ir_2(\mu\text{-CO})(CO)_2[pyrCH(P(C_6H_5)_2)_2][BF_4]_2$	MeCOMe	28.1		129
$Ir(CO)[pyrCH(P(C_6H_5)_2)_2][BF_4]$	CH_2Cl_2	~30		129
$Ir_2(CO)_2(I)[pyrCH(P(C_6H_5)_2)_2][BF_4]$	CH_2Cl_2	8.83, 18.5, 31.6, 39.2		129
$[pyrP(C_6H_5)_2Fe(CO)_3]_2$	CD_2Cl_2/298	76.2		73
W(NIPHOS)$(CO)_5$[a]	$CDCl_3$	160.5	273 ($^1J_{PW}$)	68
W(NIPHOS)$(CO)_4$[a]	$CDCl_3$	205.2	271 ($^1J_{PW}$)	68
Cr(NIPHOS)$(CO)_5$[a]	$CDCl_3$	208.6		68
$Os_3(CO)_{10}(\mu\text{-}3)$	CD_2Cl_2	5.6		169
$Os_3(CO)_{11})(3)$	$DCCl_3$	4.2		169
$Os_3(CO)_{10}(5)$	CD_2Cl_2	12.7		169
$Os_3(CO)_{10}(\mu\text{-}4)$	CD_2Cl_2	8.4 11.0		169
NiBr(2,4,6-$Me_3C_6H_2$)[2-pyr$CH_2P(C_6H_5)_2$]	C_6H_5Me	30		138
Zn{2,6-pyr$[CH_2O(CH_2)_3P(C_6H_5)_2]_2\}(CF_3SO_3)_2$	CH_2Cl_2	−9.5		46
ZnCl(μ-Cl)Rh(CO){2,6-pyr$[CH_2O\text{-}(CH_2)_3P(C_6H_5)_2]_2\}(CF_3SO_3)$	CH_2Cl_2	26.4	119	46
Cr(NIPHOS)$(CO)_4$[a]	$CDCl_3$	249.6		68
	C_6D_6	247		68

[a] NIPHOS (38) = 2-(2-pyridyl)-4,5-dimethylphosphorin.

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-C_{pyr}		
2-pyrP(C_6H_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_6H_2(*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_6H_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)	2.465(2) 2.471(2) 2.429(2) 2.404(2)				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	2.298(4)		2.399(7)				1.86(1)	1.83 [Rh-CO]	141
Rh_2(form)$_2$(μ-**3**)(CF_3CO_2)$_2$	Rh(1) Rh(2)	2.267(1) 2.269(2)	2.050(4)–2.139(4) 2.139(4)				2.5406(6)	1.834(6)	2.407(4) [Rh-O] 2.327(4) [Rh–O]	142
(η^5-C_5H_5)Rh(μ-CO)(μ-**3**)-Rh(CO)Cl	Rh(1) Rh(2)	2.222(2)	2.107(8)	2.346(3)			2.648(1)	1.877(9)	1.925(12) [Rh–Cp*]	143
(η^5-C_5H_5)Rh(μ-I)(μ-**3**)Rh(CO)I_2	Rh(1) Rh(2)		2.153(5)	2.630(1) 2.648(1) 2.647(1) 2.812(1)	91.9(1)		2.686(1)	1.832(6)	1.847(8) [Rh–Cp*] 1.811(8) [Rh–CO]	143
RhPd(μ-**3**)$_2$(CO)Cl_3	Rh	2.243(3)	2.16(1)	2.399(3) 2.499(4)	92.6(1) 87.5(1)	178.1(3)	2.594(1)	1.823(4)	1.82(1) [Rh–CO]	110, 121
	Pd	2.220(4)	2.13(1)	2.393(4)	88.4(1)	177.9(3)		1.835(4)		
PdMo(μ-**3**)$_2$(μ-CO)(CO)$_2$-Cl_2·0.5CH_2Cl_2	Pd	2.221(2)	2.113(5)	2.391(2) 2.165(6)	95.14(7)	173.4(1)	2.817(1)	1.844(6)	176.68(6) [Mo–Pd–Cl] 158.26(5) [Cl–Mo–Pd]	112, 144
	Mo	2.559(2)	2.320(5)	2.487(2)	91.31(6)	95.5(1)		1.827(6)		
[(*t*-buNC)$_2$$Cl_2$Rh($\mu$-**3**)-Pd($\mu$-Cl)]$_2$	Rh		2.10(2)	2.520(7) 2.380(6)			2.612(3)	1.82(3)		107
	Pd	2.185(6)		2.388(7) 2.479(9)	94.6(3)					
(C_6H_{12})Rh(μ-Cl)(μ-**3**)-PdCl_2·CH_2Cl_2	Rh Pd	2.246(9)	2.05(2)	2.399(8)			3.210(4)	1.93(3)		107
[(η^5-C_5H_5)Rh(μ-DMA)(μ-**3**)Rh-(CO)(μ-Cl)]$_2$·CH_2Cl_2	Rh(1)		2.133(4)	2.516(1) 2.670(1)			2.661(1)		1.919(9) [Rh–Cp*] 1.822(6) [Rh–CO]	145
	Rh(2)	2.220(1)								
Ru_3(μ-η^2-C(O)C_6H_5)[μ_3-η^2-Ppyr(C_6H_5)](CO)$_9$	Ru(1)		2.165(8)				2.821(1)		2.877(1) [Ru(1)–Ru(3)]	146
	Ru(2)	2.356(2)							3.639(1) [Ru(2)–Ru(3)]	
	Ru(3)	2.385(2)								
Ru_3[μ-η^2-C(O)C_6H_5](μ_3-η^2-Ppyr)(CO)$_6$[P(C_6H_5)$_3$]	Ru(1)		2.158(3)				2.842(1)		2.883(1) [Ru(1)–Ru(3)]	146
	Ru(2)	2.369(1) 2.405(1)							3.671(1) [Ru(2)–Ru(3)] 106.36(4) [P–Ru(2)–P]	
	Ru(3)	2.402(1)								
cis-Pd(4)$_2$$Cl_2$	Pd	2.2469(18) 2.2569(13)		2.3573(14) 2.3485(22)	168.73(11) 83.91(6) 85.82(8) 167.87(8)			1.835(13)	100.46(6) [P–Pd–P] 91.86(6) [Cl–Pd–Cl]	69
cis–Pd(4)$_2$$Cl_2$·$C_6H_6$	Pd	2.2624(8) 2.2623(8)		2.3495(9) 2.3550(9)	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

cis-Pd(4)$_2$(2-pyrH)Cl$_2$·C$_6$H$_6$	Pd	2.2433(8)		2.3807(9) 2.3498(8)	90.47(3) 177.07(16)			1.829(9)	1.980(3) [Pd–Cl] 91.04(3) [Cl–Pd–Cl]	69
[Pd[(C$_6$H$_5$)$_2$P(2,6)pyrP(O)-(C$_6$H$_5$)$_2$]Cl$_2$]$_2$	Pd	2.228(2)		2.411(3) 2.425(3) 2.324(2) 2.268(2)	78.41(24) 95.24(10) 88.34(10) 86.86(10)			1.812(12)	1.479(6) [P–O]	69
[(dpm)Rh(Cl)(CH$_2$pyrP(C$_6$H$_5$)-(CH$_2$)$_2$Ppyr(C$_6$H$_5$)]Cl·CH$_2$Cl$_2$	Rh	2.206(1) 2.261(1)		2.415(1)	169.83(4) 90.60(4)				2.023(3) Rh–C 1.510(4) N–C(–Rh)	147
Re$_2$[μ-P(C$_6$H$_5$)$_2$](μ-η^1,η^4-CHP(C$_6$H$_5$)$_2$pyr)(CO)$_7$	Re(1) Re(2)	2.520(2) 2.429(2) 2.541(2)	2.228(5)			75.6(2) 87.7(2)	4.189(0)		2.318(7) Re–CH 1.825(7) P–CH	148
Pd$_2$I$_2$(3)$_2$·0.5C$_3$H$_6$O	Pd(1) Pd(2)	2.217(1) 2.206(1)	2.121(4) 2.103(4)	2.6958(5) 2.6954(6)	97.48(4) 98.54(4)	169.4(1) 171.2(1)	2.5970(5)	1.823(5) 1.827(5)		111
Pd$_2$Cl$_2$(5)$_3$(μ-DMAD)·2CH$_2$Cl$_2$	Pd(1) Pd(2)	2.2434(9) 2.2260(9)	2.128(3) 2.127(3)	2.373(1) 2.384(1)	95.71(4) 98.71(4)	174.81(8) 171.57(8)		1.845(4) 1.860(3)		111
Pd$_3$(2,6-pyr[P(C$_6$H$_5$)$_2$]$_2$)$_3$-Cl$_6$·*n*-CH$_2$Cl$_2$	Pd								only perspective drawing shown	108
Rh$_2$Sn$_2$(CO)$_2$Cl$_6$[2,6-pyr-(P(C$_6$H$_5$)$_2$)$_2$]$_2$·2CH$_2$Cl$_2$	Rh(1)	2.349(5) 2.330(5)		2.489(5) 2.387(6)	86.6(2) 88.4(2) 87.6(2) 95.9(2)		2.601(2)		173.2(2) [P–Rh–P] 97.5(2) [Cl–Rh–Cl] 1.85(2) [Rh–CO]	149
	Rh(2)	2.304(5) 2.288(6)					2.588(2) 2.587(2)		1.92(2) [Rh–CO] 137.1(2) [P–Rh–P]	
	Sn(1)		2.62(1) 2.42(1)	2.421(5)			2.601(2) 2.588(2)		171.4(9) [N–Sn–N]	
	Sn(2)			2.409(6) 2.400(5) 2.408(5)			2.587(3)		91.3(2) [Cl–Sn–Cl] 92.5(2) [Cl–Sn–Cl] 99.7(2) [Cl–Sn–Cl]	
[μ-2,6-pyr(P(C$_6$H$_5$)$_2$)$_2$]$_2$Rh$_4$-(μ-CO)-(CO)$_2$(μ-Cl)$_2$Cl$_2$·2CH$_2$Cl$_2$·2N$_2$	Rh(1) Rh(2)			2.390(6) 2.355(4) 2.555(5) 1.88(2) 1.97(2)			2.921(2) 2.594(2)		168.0(1) [Rh(1)–Rh(2)–Rh(2′)]	108, 149
[Rh$_2$[μ-2,6-pyr(P(C$_6$H$_5$)$_2$)$_2$]$_2$-(CO)(CH$_3$OH)Cl]$^+$	Rh(1) Rh(2)	2.313(4) 2.314(4) 2.333(4) 2.329(4)		2.321(6)			5.425(2)		1.78(1) [Rh–CO] 1.809(16) [Rh–CO]	150
AuCl(3)	Au	2.286(4)		2.234(4)	178.0					151
AuCl(5)	Au	2.214(4)		2.277(5)	179.5(1)			1.84(1)	114.0(6) [Au–P–C] 114.4(5) [Au–P–C′]	152
{Ru[5-PO][2-pyr]$_2$P(O)O]}-[BF$_4$]·2H$_2$O	Ru		2.04(3)–2.11(3)							153
Zn(5)(NO$_3$)$_2$	Zn		2.050(3) 2.047(3) 2.253(3)							154
Zn(5)$_2$[ClO$_4$]$_2$	Zn		2.178(4) 2.152(4)							154
[Ru(5)$_2$](tos)$_2$·C$_2$H$_5$OH	Ru		2.06(1)–2.09(1)					1.80(2)–1.85(2)		155
rac-{[(C$_6$H$_5$)pyrP]$_2$CH$_2$}[Rh-(CO)Cl$_2$]$_2$·2MeCN	Rh(1) Rh(2)	2.212(2) 2.219(2)	2.134(5) 2.148(5)	2.393(2) 2.379(2)	176.46(8) 175.76(8)	91.9(1) 93.4(1)	3.093(1)	1.837(6) 1.854(6)	1.797(6) [Rh–CO] 1.808(6) [Rh–CO]	19
meso-{[(C$_6$H$_5$)pyrP)$_2$(CH$_2$)$_3$]-Rh$_2$Cl$_2$}[Rh(CO)$_2$Cl$_2$]$_2$	Rh(1)			2.336(4) 2.335(4)			2.650(1)	1.829(9)	1.79(1) [Rh–CO] 1.81(1) [Rh–CO]	19
	Rh(2)	2.244(3) 2.261(2)	2.193(6) 2.185(7)	2.511(2)	85.34(9) 86.29(8)	174.8(2) 94.2(2) 175.9(2)		1.814(9)		

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}		
$Rh_2\{\mu$-[2,6-pyr($P(C_6H_5)_2)_2\}_2$-(μ-CO)(μ-I)][$B(C_6H_5)_4$·$2CH_2Cl_2$	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]	123
		2.238(3)				69.8(3)		1.861(10)	107.4(1) [P–Rh–P]	
	Rh(2)	2.303(3)	2.106(10)	2.919(2)	93.8(1)	176.8(3)	2.577(2)	1.854(14)	2.04 [Rh–CO]	
		2.251(4)				69.7(3)		1.868(12)	107.1(1) [P–Rh–P]	
$Pt_2\{[\mu$-$(C_6H_5)_2P]_2pyr\}_2Cl_2$·$6CH_2Cl_2$	Pt	2.252(7)		2.356(7)	176.6(2)			1.828(26)	88.4(2) [Cl–Pt–Cl]	77
		2.278(7)		2.363(7)	86.5(2)				96.2(2) [P–Pt–P]	
					89.2(2)					
					171.6(2)					
$Pt_2\{[\mu$-$(C_6H_5)_2P]_2pyr\}_2I_4$·$2CH_2Cl_2$	Pt	2.307(4)		2.602(1)	93.2(1)			1.840(18)		77
		2.306(5)		2.607(1)	89.8(1)					
					87.3(1)					
					90.0(1)					
[Pt(**3**)$_2$Cl][Rh(CO)$_2$Cl$_2$]·0.5CH_2Cl_2	Pt	2.223(6)	2.07(2)	2.340(5)	166.8(2)	70.8(5)		1.84(2)	91.7(2) [Cl–Rh–Cl]	113
		22.32(6)		2.353(5)	92.2(2)	171.1(5)		1.86(2)	1.79(2), 1.86(2) [RhCO]	
	Rh			2.342(6)						
Rh_2(**3**)$_2(\mu$-CO)Cl_2	Rh(1)	2.206(1)	2.116(5)	2.355(1)	91.9(.1)	172.0(.1)	2.612(1)	1.831(6)	84.3 [Rh–C–Rh]	121, 124
	Rh(2)	2.215(1)	2.114(5)	2.355(1)	93.3(.1)	177.8(.1)				
$Cu_2(\mu$-**3**$)_3$(MeCN)[BF_4]$_2$	Cu(1)	2.196(2)	2.056(6)			132.3(2)	2.721(3)	1.842(6)		137
			2.048(4)			127.7(2)		1.838(7)		
	Cu(2)	2.310(3)	2.089(5)			108.5(1)		1.832(7)		
		2.274(2)	2.114(4)			116.6(1)				
						97.7(2)				
						97.8(2)				
PtMo(μ-**3**$)_2(\mu$-CO)(CO$)_2Cl_2$·	Pt	2.348(5)		2.324(4)	95.5(2)		2.845(1)		166.1(2) [P–Pt–P]	119
0.406CH_2Cl_2		2.227(5)			93.4(2)				2.218(17) [Pt–CO]	
	Mo		2.301(17)	2.521(4)					1.907(20) [Mo–CO]	
			2.315(12)						1.950(18) [Mo–CO]	
									1.954(17) [Mo–CO]	
Mo_2(**3**$)_2$(Cl$)_2$(AcO$)_2$·$2CH_2Cl_2$	Mo	2.5341(7)	2.240(2)	2.7544(7)	79.12(2)	165.72(8)	2.1900(3)	1.844(3)	2.110(3), 2.116(3) [Mo–O]	156
$Mo_2(\eta$-$C_6H_5)_2$(CO$)_4$(**3**$)_2$·$2Et_2O$	Mo	2.412(6)					3.276(3)	1.83(2)	1.96 [Mo–CO]	132
(η^5-C_5H_5)(*t*-buNC)Rh(μ-**3**)Pd-	Rh	2.241(2)					2.631(1)	1.820(6)		115
(*t*-buNC)(Cl)PF_6·C_6H_6·MeOH	Pd		2.112(6)	2.406(2)						
PdW(μ-**3**$)_2(\mu$-CO)(CO$_2$)Cl$_2$·	W	2.541(2)	2.281(6)	2.480(2)	90.73(6)	95.0(1)	2.8119(5)	1.839(7)		157
0.7CH_2Cl_2	Pd	2.205(2)	2.142(6)	2.387(3)	91.4(2)	173.6(2)		1.853(7)		
Co(**3**PO$)_2Cl_2$	Co		2.134(5)	2.305(2)				1.835(7)	2.23(1) [Co–CO]	85
			2.134(5)	2.305(2)					1.30(2) [P–O]	
Co(**4**)Cl_2·$^1/_2$EtOH	Co		2.031(2)	2.221(1)					94.8(1) [N–Co–N]	158
									116.2(1) [Cl–Co–Cl]	
Co(0)Co(**I**)(μ-**3**$)_2(\mu$-CO)(CO)Cl	Co(1)		2.137(7)	2.238(3)			2.441(2)	1.873(8)	143.33(7) [Co–Co–Cl]	159
			2.100(6)							
	Co(2)	2.177(3)						1.867(8)		
		2.182(2)								
Co(**I**)Co(**II**)(μ-**3**$)_2(\mu$-CO$)_2Cl_3$	Co(1)	2.305(10)		2.374(4)	94.1(4)		2.685(1)	1.83(2)		160
		2.32(2)			88.7(3)					
	Co(2)		2.248(14)	2.485(4)				1.84(3)		
			2.17(2)	2.461(13)						
cis-$Re_2(\mu$-AcO$)_2Cl_2(\mu$-**3**$)_2$[PF_6]	Re(1)	2.401(6)	2.13(1)	2.506(5)	83.6(2)	91.7(5)	2.261(1)			161
	Re(2)	2.406(5)	2.16(2)	2.532(5)	85.7(2)	97.7(4)				
Re_2Cl_3(**3**$)_2$[(C_6H_5)(C_6H_4)Ppyr]	Re(1)	2.388(9)	2.08(2)	2.578(9)	85.3(3)	163.3(3)	2.336(2)	1.80(3)–1.84(3)	85.0(3) [Cl–Re–Cl]	23, 134
		2.359(10)		2.429(9)	96.3(3)	98.1(7)		1.84(3)	98.3(3) [P–Re–P]	
					80.5(3)					
					165.3(3)					
	Re(2)	2.354(9)	2.17(3)	2.568(9)	82.8(3)	170.5(7)			2.16(3) [Re–C]	
			2.22(3)			92.1(6)				

$Re_2Cl_2(3)_4[PF_6]_2 \cdot 2Me_2CO$	Re(1)	2.436(5)	2.19(2)	2.575(5)	86.3(2)	91.1(4)	2.300(1)	1.82(2)–1.83(2)	174.4(2) [P–Re–P]	23
		2.429(5)	2.210(15)		88.0(2)	87.9(4)		1.83(2)	169.5(6) [N–Re–N]	
						88.1(2)				
						91.9(4)				
	Re(2)	2.428(6)	2.18(2)	2.628(6)	88.1(2)	91.4(5)			174.0(2) [P–Re–P]	
		2.433(6)	2.227(15)		86.0(2)	87.2(4)			169.3(6) [N–Re–N]	
						92.8(5)				
						87.6(5)				
$Re_2Cl_4(3)_2(PEt_3)$	Re(1)	2.365(2)	2.206(7)	2.616(2)	77.50(8)	92.0(2)	2.270(1)	1.829(8)–1.84(9)	89.65(8) [Cl–Re–Cl]	23
		2.480(3)		2.406(2)	84.08(9)	162.9(2)		1.84(9)	100.25(9) [P–Re–P]	
					165.40(8)					
					85.07(5)					
	Re(2)	2.346(2)	2.076(7)	2.355(2)	87.30(9)	93.5(2)			85.1(1) [Cl–Re–Cl]	
				2.387(2)	154.75(9)					
$Os_2(AcO)(3)_2Cl_4 \cdot 2CH_2Cl_2$	Os(1)	2.329(5)	2.09(2)	2.428(6)	83.6(2)	90.8(4)	2.395(1)	1.82(2)	2.10(1) [Os–O]	162
				2.377(6)					87.9(2) [Cl–Os–Cl]	
	Os(2)	2.331(6)	2.06(2)	2.421(6)	83.3(2)	90.2(1)		1.81(2)	2.10(1) [Os–O]	
				2.365(6)	169.4(2)				88.6(2) [Cl–Os–Cl]	
$Os_2(AcO)(3)_2Cl_4 \cdot 2Me_2CO$	Os(1)	2.332(2)	2.066(6)	2.362(2)	84.23(8)	90.6(2)	2.388(1)	1.834(8)	2.096(5) [Os–O]	162
				2.436(2)	169.13(7)				86.91(8) [Cl–Os–Cl]	
	Os(2)	2.338(2)	2.060(6)	2.433(2)	84.09(7)	90.9(2)		1.831(8)	2.110(5) [Os–O]	
				2.371(2)	170.16(8)				88.42(7) [Cl–Os–Cl]	
$Rh_2(AcO)_2(3)_2Cl_2$	Rh(1)	2.212(3)	2.046(10)	2.538(3)	97.8(1)	91.2(3)	2.518(1)	1.853(11)		162
	Rh(2)	2.220(3)	2.068(9)	2.537(3)	97.3(1)	90.9(3)		1.847(13)		
$UO_2(NO_3)_2[(C_6H_5)_2P(O)]pyrO$	U							1.82(1)	2.41(1) U–O(P)	86
									2.38(1) U–O(N)	
$Mo_2(NCS)_4(3)_2 \cdot 2THF \cdot 2(C_6H_6CH_3)$	Mo	2.545(2)	2.288(5)			96.2(2)	2.191(1)		2.086(5) Mo–N(CS)	163
$Mo_2[(C_6H_5)_2Ppyr(6\text{-}O^-)]_4$	Mo						2.103(1)			116
$[Ag(3)Cl]_4$	Ag(1)	2.387(5)		2.538(5)	138.9(2)				1.834(16) [Cl–Ag–Cl]	164
				2.646(5)	119.2(2)					
	Ag(2)	2.396(5)		2.586(4)	132.2(2)				1.826(16) [Cl–Ag–Cl]	
				2.803(5)	114.8(1)					
	Ag(3)	2.429(5)		2.646(4)	125.8(1)				1.824(16) [Cl–Ag–Cl]	
				2.721(5)	130.2(1)					
	Ag(4)	2.404(5)		2.628(4)	130.6(1)				1.828(16) [Cl–Ag–Cl]	
				2.709(4)	118.4(1)					
$Ag_2(3)_3Cl_2$	Ag(1)	2.432(3)		2.618(2)	110.0(1)		3.074(2)	1.85(1)	98.1(1) [Cl–Ag–Cl]	151
		2.452(3)		2.701(4)	106.25(9)					
					112.70(9)					
					100.7(1)					
	Ag(2)	2.436(4)	2.451(9)	2.638(4)	112.1(1)	126.7(2)			100.23(1) [Cl–Ag–Cl]	
				2.601(9)	107.4(1)					
$RuPd(3)_2(CO)_2Cl_2 \cdot 1.25CH_2Cl_2$	Ru	2.396(2)	2.178(5)	2.477(2)	100.6(1)	91.1(1)	2.660(1)	1.836(6)		22
	Pd	2.190(2)	2.126(5)	2.426(2)	99.4(1)	167.3(1)		1.838(6)		
$Ru(3)(CO)_2Cl_2$	Ru	2.322(2)	2.119(6)	2.408(2)	160.4(1)	68.7(2)		1.859(8)	1.877(8), 1.874(8) [Ru–CO]	70
				2.417(2)	88.8(1)					
$[Au(2\text{-}pyrPMe_2)]_2[BF_4]$	Au	2.215(6)	2.086(16)			176.1(5)	2.776(1)	1.83(2)	87.1(1) [Au–Au–P]	18
									115.3(7) [Au–P–C]	
$PtRh[\mu\text{-}P(C_6H_5)_2](\mu\text{-}pyrCH[P(C_6H_5)_2]_2)$-	Pt	2.324(3)					2.708(1)		73.8(1) [Pt–P–Rh]	127
$(pyrCH_2P(C_6H_5)_2)(P(C_6H_5)_3)[BF_4]_2$		2.287(3)								
		2.315(3)								
	Rh	2.276(3)	2.19(1)			151.4(3)			88.0(4) [N–Rh–N]	
		2.381(3)	2.12(1)			86.6(3)			110.4(1) [P–Rh–P]	
		2.282(3)				79.4(3)			102.5(1) [P–Rh–P]	
						166.7(3)			105.9(1) [P–Rh–P]	
						96.1(3)				
						79.4(3)				

Table 8 (Continued)

crystal structures[a]	metal	bond distances (Å) M-P	M-N	M-X	bond angles (deg) X-M-P	N-M-P	distance (Å) M-M′	P-C_{pyr}	miscellaneous distances (Å) or angles (deg)	ref(s)
$\{Rh_2[pyrCH(P(C_6H_5)_2)]_2(CO)_2\}[PF_6]_2 \cdot C_3H_6O$	Rh	2.271(1)	2.187(5)			77.2(1)	3.054(1)		1.819(6) [Rh–CO]	129
		2.358(1)				99.5(2)			176.70(6) [P–Rh–P]	
Rh(CO)ZnCl(μ-Cl){2,6-pyr[CH_2O-$(CH_2)_3P(C_6H_5)_2$]$_2$}(CF_3SO_3)	Rh	2.331(5)		2.399(4)	91.4(2)		4.002(1)		174.0(2) [P–Rh–P]	46
		2.325(4)			89.8(2)				114.5(2) [Rh–P–Zn]	
	Zn		2.00(1)	2.360(4)					2.22(1) [Zn–O]	
				2.201(6)					2.23(1) [Zn–O]	
$Ir_2(\mu\text{-CO})(CO)_2[pyrCH(P(C_6H_5)_2)]_2[BF_4]_2$	Ir(1)	2.319(5)	2.32(1)			77.2(1)	2.815(1)		172.0(2) [P–Ir–P]	129
		2.348(5)				100.3(4)				
	Ir(2)	2.355(5)	2.32(1)			73.4(5)			171.3(2) [P–Ir–P]	
		2.325(5)				100.0(4)				
$RhAu[pyrCH(P(C_6H_5)_2)_2[BF_4NO_3]$	Rh	2.207(7)	2.18(2)			176.1(5)	2.850(2)		103.9(3) [P–Rh–P]	128
		2.227(6)	2.14(2)			174.9(7)			99.9(80) [N–Rh–N]	
						77.5(7)				
						78.9(6)			170.3(3) [P–Au–P]	
	Au	2.295(6)								
		2.285(7)								
$Rh_2(CO)[\mu\text{-pyrCH}(P(C_6H_5)_2)_2]_2$-$[B(C_6H_5)_4]_2 \cdot 2CH_2Cl_2$	Rh(1)	2.297					2.674(1)		172.5(2) [P–Rh–P]	126
		2.318							1.78 [Rh–CO]	
	Rh(2)	2.238	2.14			174.6(3)			102.1(2) [P–Rh–P]	
		2.228	2.15			173.4(3)				
						77.1(3)				
						82.5(3)				
$Ni(3)_2(CO)_2$	Ni	2.213(1)						1.846(4)	1.757(6) [Ni–CO]	165
		2.220(1)						1.839(5)	1.787(5), 112.87(5) [P–Ni–P]	165
Ni[P(2,6-pyrCH=NO)$_3$BF][BF_4]	Ni	3.452(3)	2.030(21)[b]					1.836(10)	3.089(11) [Ni–B]	97
			2.043(20)[c]					1.826(10)	1.376(17) [B–F]	
								1.850(10)		
Fe[P(2,6-pyrCH=NO)$_3$BF][BF]$\cdot CH_2Cl_2$	Fe	3.445(03)	1.931(11)[b]					1.835(13)	3.035(12) [Fe–B]	99, 166
			1.978(06)[c]						1.362(18) [B–F]	
Co[P(2,6-pyrCH=NO)$_3$BF][BF_4]$\cdot CH_3CN$	Co	3.428(8)	2.063(18)[b]					1.811(23)	3.196(34) [Co–B]	100, 167
			2.118(36)[c]					1.823(26)	1.284(38) [B–F]	
								1.928(25)		
Zn[P(2,6-pyrCH=NO)$_3$BF][BF_4]	Zn	3.399(3)	2.099(18)[b]					1.854(10)	3.078(15) [Zn–B]	168
			2.071(22)[c]					1.837(9)	1.383(16) [B–F]	
								1.842(9)		
Cr[NIPHOS](CO)$_4$	Cr	2.280(1)	2.193(4)			76.7(1)			1.928(7), 1.889(7) [Cr–CO]	68
									1.825(5), 1.843(5) [Cr–CO]	
[PtCl(NIPHOSH·OMe)(PMe_3)][SbF_6]	Pt	2.189(1)	2.153(4)	2.354(1)	71.6(05)	83.8(.11)				79
		2.250(1)			87.5(05)	170.6(.11)				
[$Ir_2(COD)_2$(NIPHOS$_2$)][SbF_6]	Ir(1)	2.424(2)	2.128(12)			80.6(3)	2.894(1)		74.1(1), 74.2(1) [Ir–P–Ir]	130
		2.377(4)				86.3(3)				
	Ir(2)	2.371(3)	2.098(12)			86.3(3)				
		2.424(4)				80.8(3)				
$Os_3(CO)_{10}(\mu\text{-}3)$	Os(1)	2.380(4)					2.827(2)	1.85(2)	1.92(2) [Os–CO]	169
	Os(2)		2.22(1)				2.872(2)		1.87(2) [Os–CO]	
	Os(3)						2.929(2)		2.01(2), 1.94(2) [Os–CO]	
Cr(NIPHOS)(CO)$_4$	Cr	2.280(1)	2.193(4)			76.7(1)			1.825(5), 1.843(5) [Cr–CO]	130
									1.889(7), 1.928(7) [Cr–CO]	

[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(aldoximo) 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-[$(C_6H_5)_2PCH_2$]C_5H_4N}[(1,2,3-η)-3-(CH_2=$CHCMe_2$)]Pd[BF_4] was prepared and shown, via NMR spectral data, to isomerize in solution.[179]

When **5** was treated with [$Ru_3(CO)_{12}$] at room temperature in THF and a catalytic amount of N{[P-($C_6H_5)_3]_2$}Cl was added, {$Ru_3(\mu$-2-pyr)[μ_3-(2-pyr)-P](CO)$_9$} was formed. The proposed intermediates [$Ru_3(CO)_n$(**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**)(C_6H_5C≡$C)_2$] with 2 equiv of [Cu (or Ag) $(MeCN)_4]^+$ afforded {Pt(**3**)(C_6H_5C≡$C)_2$-[Cu$(MeCN)_2]_2$}[$PF_6]_2$ or {Pt(**3**)$_2$(C_6H_5C≡$C)_2$-[Ag(MeCN)]$_2$[$PF_6]_2$ in high yield; their photophysics and electrochemistry have been determined.[181]

Reaction of [$Rh_2(\mu$-CO)Cl_2(**3**)$_2$] with $NaBH_4$ gave $Rh_2(\mu$-CO)$(BH_4)_2$(**3**)$_2$, which was characterized by a crystal structure and shown to catalyze ethylene hydrogenation.[182]

Bifunctional 2-[$(C_6H_5)_2P$(O)$CH_2(C_5H_4N$(O)] and trifunctional 2,6-[$(C_6H_5)_2P$(O)$CH_2]_2C_5H_3N$(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$(CH_2)_2$P-(C_6H_5)$(CH_2)_3$Y [Y = OEt; OC_6H_5; NHC_6H_5; NHC_6H_{11}] in the presence of $TlPF_6$ (a halogen scavenger) at 0 °C gave {Rh(COD)[2-pyr$(CH_2)_2$P(C_6H_5)$(CH_2)_3$Y][PF_6]}, which catalytically polymerizes phenylacetylene to polyacetylene with improved selectivity and larger M_w values over previous catalysts.[184]

An [$Os_3(CO)_{10}(\mu$-**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*-[$Pt(DMSO)_2Cl_2$] with **3** afforded *cis*-[Pt(DMSO)(**3**)Cl_2], which possesses a square planar Pt^{II} center and an η^1-P–Pt bond. *cis*-[Pt(DMSO)-(**3**)Cl_2] 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 [$Pt_2(\mu$-**3**)$_2Cl_2$](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 $CdBr_2$ afforded [$(MeO)_3Si$]$(CO)_3$-Fe(μ-**3**)$]_2$Cd(μ-Br)$\}_2$, which with 4-picoline gave {[$(MeO)_3Si$](CO)$_3$Fe(μ-**3**)CdBr(4-pic)}, whereas K{$Fe(CO)_3$[$Si(OMe)_3$](**3**)} with $CdBr_2$ afforded *mer*-{[$(MeO)_3Si$](CO)$_3$Fe(μ-**3**)$\}_2$Cd.[187]

The acyl complex $Ru_3[\mu$-C(O)(C_6H_5)][μ_3-η^2-P(C_6H_5)(2-pyr)](CO)$_9$ with 3 equiv of $PH(C_6H_5)_2$ and $Ru_3[\mu_3$-η^2-P(C_6H_5)(2-pyr)][μ-P($C_6H_5)_2$](CO)$_6(\mu$-CO)$_2$ with 2 equiv of $PH(C_6H_5)_2$ both gave $Ru_3[\mu_3$-η^2-P(C_6H_5)(2-pyr)][μ-P($C_6H_5)_2]_3$(CO)$_6$, by the incorporation of a [$(C_6H_5)_2$P] 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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