Journal of the Chinese Chemical Society, **1992**, *39*, 611-616

Tripodal Phosphine Ligands. Syntheses and Coordination Chemistry Toward Mn(I)

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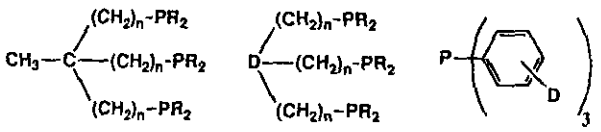
The recent development of ligand syntheses and coordination chemistry-toward manganese(I) involving tripodal phosphines is sumrnarized and discussed.

INTRODUCTION

Tripodal ligands are those donors disposed at the base of a "tripod", which provides the most characteristic arrangement for formation of mononuclear complexes with various stereochemistry.[1] However, such a feature disappears as the length of the carbon chain increases. The most suitable distance is less than two carbon units from the donor center to the connective atom. Several tripod-like phosphine polydentates[2-5] are summarized in Scheme I. Although all these tripodal ligands comprise a field under development by many research groups, this account describes recent progress on work on the tripodal system **I** with the backbone in carbon atoms, especially with the donor atom being one carbon away from the connective carbon center (n = 1 in **I**).[6]

Scheme I

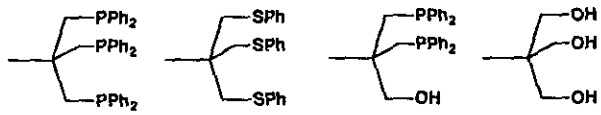
D : Donor atom



I II III

In terms of the properties of donor atoms, phosphine is considered to be a good σ-donor and moderate π-acceptor, which might stabilize various transition-metal complexes. Since the tripodal phosphine ligand 1,1,1-tris (diphenylphosphinomethyl)ethane (P_3) was reported in 1962,[2] the coordination and organometallic chemistry involving P_3 have received considerable attention, with the latest review in 1982.[1] 1,1,1-Tris(phenylthiomethyl)ethane S_3, a potential analog to phosphine but exhibting a moderate coordinating ability of sulfur atoms, has been less investigated.[7] A review concerning the nitrogen donor 1,1,1-tris(aminomethyl)ethane N_3 describes the complexation of this ligand with higher-oxidation metal complexes.[8] These tripodal ligands containing the same donors comprise the early work in this field. Chemists have become interested in not only "homo-donor" but also "heter-donor" ones, due to the versatile coordination behaviors of mixed donor systems. Despite the existence of these reviews, a summary of recent progress on work of the tripodal phosphine system and the coordination behavior toward Mn(I) is needed.

The abbreviation of tripodal ligands throughout this text is simply based on the donor atoms; the particular substituent on the donor atom is given in parentheses right after the donor atom. For example, $P_2O(H)$ indicates that the oxygen donor is a hydroxyl function.



P_3 S_3 $P_2O(H)$ 1

SYNTHESES OF TRIPODAL PHOSPHINES

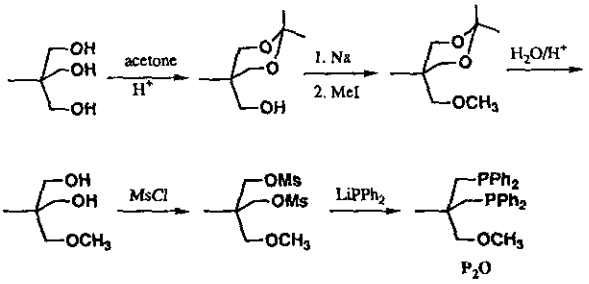
All tripodal ligands of **I** (n = 1) are based on 1,1,1-tris(hydroxymethyl)ethane **1** as a precursor, which is cheap and commercial available. The first such tripod-like phosphine P_3, reported by Hewertson and Watson,[2] was prepared from nucleophilic displacement of 1,1,1-tris(chloromethyl)ethane by sodium diphenylphosphide. This triphosphine was isolated as a white solid (mp 100-101 °C), which slowly oxidized in air. Dimethylphosphino $P_3(Me)$[9] and diethylphosphino $P_3(Et)$[10] analogues were prepared similarly. Both $P_3(Me)$ and $P_3(Et)$ are marketed commercially.

In order to prepare mixed donor ligands, one requires differentiation of functional groups among triol **1** during

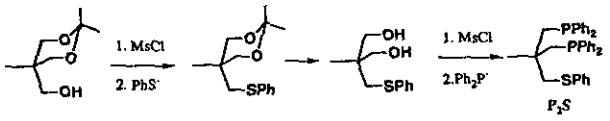
This review is invited to commemorate the sixtieth anniversary of the Chinese Chemical Society.

the synthesis. This problem is easily solved with a ketal protection procedure. Thus 2,2-bis(diphenylphosphinomethyl)-1-methoxypropane (P_2O),[11] 2,2-bis (diphenylphosphinomethyl)-1-phenylthiopropane (P_2S)[12] and 2,2-bis-(diphenylphosphinomethyl)-1-(*N*,*N*-diethylamino)propane (P_2N)[13] were prepared by a similar strategy and summarized in Schemes II, III, and IV respectively; all steps are manipulations of typical organic functional groups generally in high yields except those involving nucleophilic substitution. Due to the substituted spot being a neopentyl site, the reaction requires much more severe condition and provides only moderate yield. In P_2N, the introduction of nitrogen donor requires much effort. Thus such donor is incorporated by a sequence: (i) substitution by azide, (ii) reduction and (iii) alkylation; the direct amination accommodates a low yield for the desired product.[14]

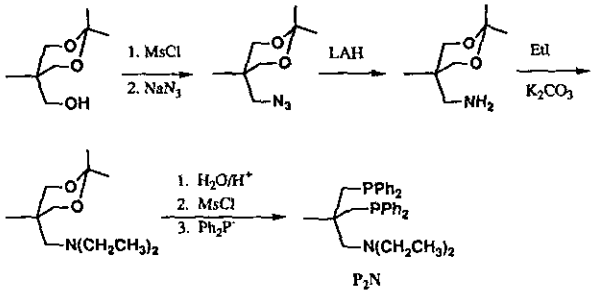
Scheme II



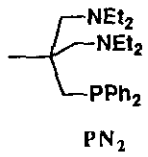
Scheme III



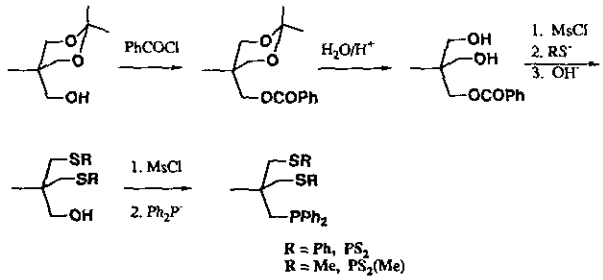
Scheme IV



The construction of the mixed polydentates depends on the synthetic sequence of the incorporation of those donor groups. All donor atoms are potential nucleophiles, which might undergo intramolecular reaction to give unnecessary side products. To avoid this problem, the deposition of donor groups follows sequence oxygen < nitrogen ~ sulfur < phosphorus. For example, the route to PS_2[15] and $PS_2(Me)$[16] is designed to attach the phenylthio group first (Scheme V); so is the amino group in PN_2.[13] Another advantage of the incorporation of phosphorus moieties at the last step of the synthesis is to save effort of handling air-sensitive phosphines.

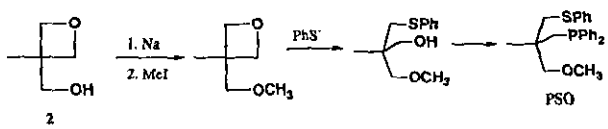


Scheme V

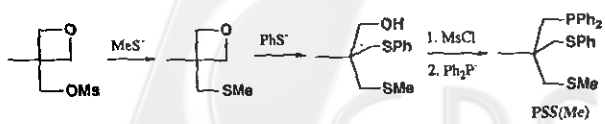


Instead of the ketal protection method, the oxetane derivative **2** is also a good source for preparation of tripodal ligands, especially for those with three different donor systems. As shown in scheme VI the synthesis of 2-(diphenylphosphinomethyl)-2-(phenylthiomethyl)-1-methoxypropane (**PSO**)[17] used **2** as starting material. The donor sites were disposed in the order ether, sulfide and phosphine. By a similar strategy, the synthetic approach to 2-(diphenylphosphinomethyl)-2-(phenylthiomethyl)-1-(*N*, *N*-diethylamino)propane (**PSN**)[18] was accomplished. Ligands with different substituents on donor atoms of the same kind such as **PSS(Me)**[19] are prepared according to

Scheme VI



Scheme VII

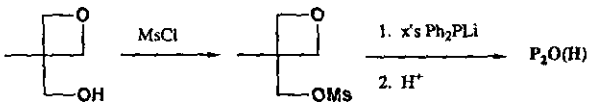


Scheme VII. However, all of these potential chiral ligands are obtained in recemic form from these synthetic routes.

The transformation of the hydroxyl function of **2** into the corresponding mesylate followed by treatment excess diphenylphosphide provides the desired compound $P_2O(H)$[20] in reasonable yield (Scheme VIII). The sulfur analog $P_2S(H)$[21] is obtained in a similar procedure from thietane **3**.

3 $P_2S(H)$

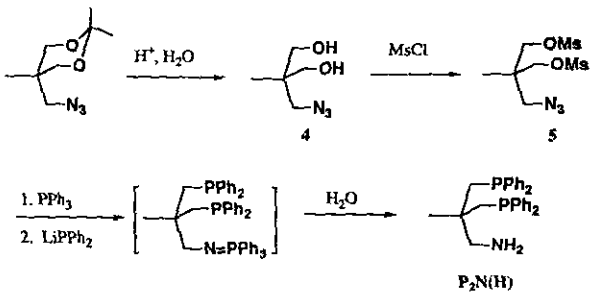
Scheme VIII



2

A convenient and short approach to a tripodal ligand containing a primary amino group was accomplished by using iminophosphorane as protecting group for a primary amine.[22] The azide alcohol **4**, obtained from the hydrolysis of azide ketal, was treated with mesyl chloride to provide the desired mesylate **5**. Conversion of **5** to the desired phosphine $P_2N(H)$ was achieved in a one-pot reaction according to the following sequence: reaction with triphenylphosphine to generate the corresponding iminophosphane; replacement of mesylate with the diphenylphosphino moiety, and removal of the iminophosphorane protecting group (Scheme IX). The route indeed saves the steps of protection and deprotection of the amino group during the synthesis.

Scheme IX

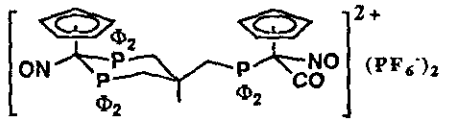


All tripodal phosphines are air-sensitive compounds and must be handled anaerobically, especially those having a dialkylphosphino moiety. Crystal structure of these free tripodal ligands has not been reported.

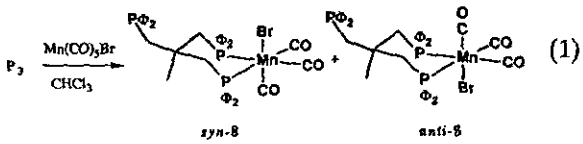
COORDINATION CHEMISTRY OF Mn(I)

Although the coordination chemistry with mixed tripodal phosphine ligands toward various transition-metal ions has been investigated,[1,12-21,23] I briefly describe here the chemistry involving Mn(I).

Ligand substitution of $[CpMn(CO)_2NO]$ with P_3 in methanol gives a dimeric manganese complex $[Cp_2Mn_2(CO)(NO)_2P_3](PF_6)_2$ **6** in which two phosphine moieties are coordinate to one metallic center in a bidentate mode and the third phosphine coordinates to the second metallic center.[24] The P_3 ligand acts in a tridentate mode in the complex $[Mn(CO)_3\{\eta^3\text{-}P_3\}][Mn(CO)_5]$ **7** resulting from the reaction of $Mn_2(CO)_{10}$ with the ligand.[25] The reaction of P_3 with $Mn(CO)_5Br$ in refluxing chloroform provides only a stereoisomeric mixture of monomeric metal complexes *syn*-**8** and *anti*-**8** (Eq. 1).[26]



6

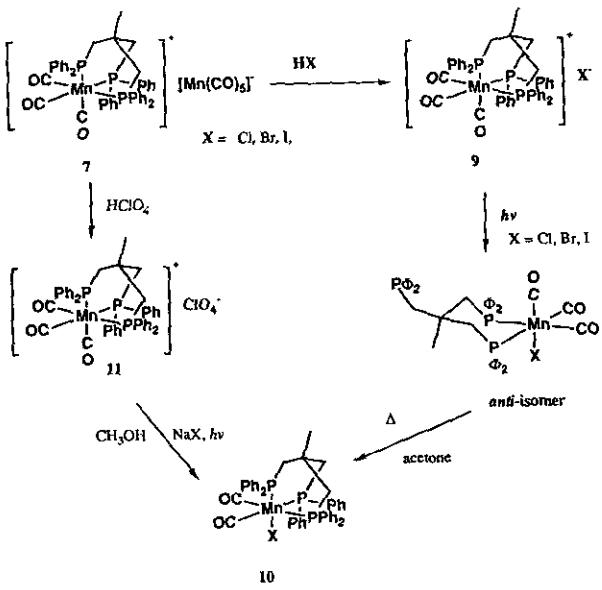


(1)

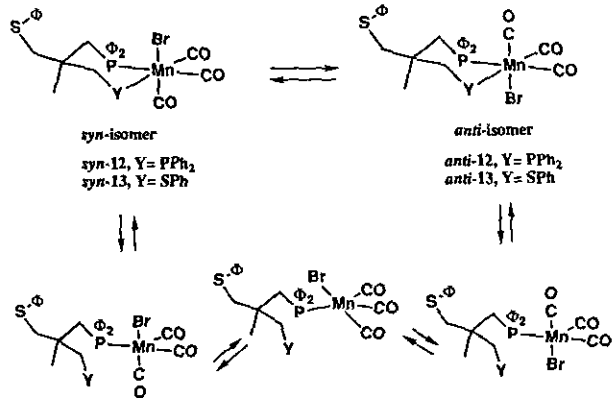
The interconversion of P_3 in a bidentate or tridentate mode with manganese(I) complexes is illustrated in Scheme X.[27-29] Anion metathesis of **7** with aqueous HX gives **9**. Upon irradiation with ultraviolet light, complexes **9** undergo dissociation of phosphine and coordination of halides to form *fac*-$[(P,P'\text{-}P_3)Mn(CO)_3X]$, in which P_3 behaves as a bidentate ligand. Thermal reaction of these complexes *fac*-$[(P,P'\text{-}P_3)Mn(CO)_3X]$ in a polar solvent results in the formation of η^3-complexes **10**. A complex of this type is attained in a simple way by the direct photo chemical reaction of **11**, generated from anion exchange of **7**, with alkali metal halides and psuedohalides MX [M = Na, K; X = Cl, Br, I, N_3, NCO] in methanolic solution.

Tripodal ligands containing various mixed donor atoms undergo complexation with $Mn(CO)_5Br$ to form *fac*-$[(\eta^2\text{-tripodal})MnBr(CO)_3$. The selectivity of donor atoms from tripodal ligands coordinating to the metal center fol-

Scheme X



Scheme XI



lows tendency phosphorus > sulfur > > nitrogen or oxygen. Thus in case of P_2S,[26] P_2N,[30] P_2O[31] and $P_2O(H)$,[20] two phosphorus atoms of each tripodal ligand coordinate to the metallic center to form *fac*-[*P,P'*-(P_2Y)$Mn(CO)_3Br$], Y = SPh, NEt_2, OMe, OH, where one phosphorus and one sulfur atoms in PS_2[26] and PSO[17] are bonded to manganese. Unlike P_3, the potential tridentate ligand P_2S reacts with $Mn_2(CO)_{10}$ does not provide the desired $[Mn(CO)_3\{\eta^3$-$P_2S\}][Mn(CO)_5]$. Under mild conditions, a dimeric species $[(PSO)Mn(CO)_3]_2$ is isolated from the reaction of $Mn_2(CO)_{10}$ with ligand PSO in chloroform. Such dimetallic species readily decomposes to yield a monomeric complex *fac*-[*P,S*-(PSO)$Mn(CO)_3Br$] upon treatment with bromine.[17] The coordination chemistry involving these tripodal phosphine ligands is similar to that of $Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$ (triphos), which also acts as bidentate in *fac*-$Br(CO)_3Mn$(triphos).[32]

Different from the most mixed tripodal ligands, PN_2 allows only bond of the phosphine moiety to the manganese(I) center without the formation of a P-N chelation complex.[31] This effect is believed due to both the weak electronic ability of the amine donor toward Mn(I) and the steric bulkiness of diethylamino moiety of that donor.

Each of complex in *fac*-[(η^2-tripodal)$MnBr(CO)_3$] form exists as a pair of stereoisomers: one is the uncoordinated donor remaining on the same side of the bromide ligand along the chelating ring (*syn* isomer); the other is on the opposite side (*anti* isomer). The conversion of these stereoisomers in both *fac*-[(*P,P'*-P_2S)$MnBr(CO)_3$ and *fac*-[(*P,S*-PS_2)$MnBr(CO)_3$ was carefully investigated (Scheme XI).[26]

In *fac*-[(*P,P'*-P_2S)$MnBr(CO)_3$, both isomers (*syn*-**12** and *anti*-**12**) were isolated and their structures confirmed by analysis of a single crystal.[26] The ^1H NMR chemical shifts of methyl groups in both isomers proved an uniquely distingishing characteristic. In general the shift of the methyl group in *syn* isomer is more upfield by about 0.5 ppm than that in the *anti* isomer. The equilibrium between *syn*-**12** and *anti*-**12** is in the ratio of 3:2. Hence *syn*-**12** is more stable than the *anti*-**12** by only 1 kJ mol^{-1}. The equilibrium constant for *fac*-[(*P,S*-PS_2)$MnBr(CO)_3$] is unity, indicating both isomers to have the same energy. Activation parameters obtained from kinetic studies of isomerization of *syn*-**12** to *anti*-**12** are $\Delta H^{\neq}$ = 130 KJ mol^{-1} $\Delta S^{\neq}$ = 46 J K^{-1} mol^{-1}; whereas $\Delta H^{\neq}$ = 105 KJ mol^{-1}, $\Delta S^{\neq}$ = 8 J K^{-1} mol^{-1} for *fac*-[(*P,S*-PS_2)$MnBr(CO)_3$. The bond strength of Mn-P is stronger than Mn-S by about 25 kJ mol^{-1}.[26] This result is consistent with the isomerization following the mechanism shown in Scheme XI; dissociation of one donor (phosphorus in P_2S; sulfur in PS_2) gives the pentavalent intermediate, which is rapidly converted into another isomer, followed by re-coordination.

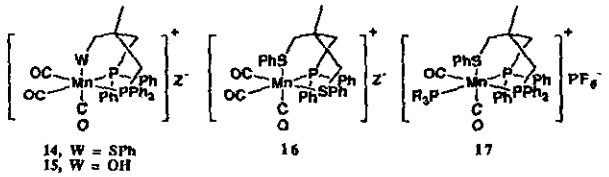
About the conformation of the chelating ring in *syn*-**12** and *anti*-**12**, a chair form is adopted for *syn*-**12** in the solid state but the boat form for *anti*-**12**. In both cases, as with other (L-L)$Mn(CO)_3Br$ complexes, the bromide ligand is favored to point over the chelating ring, due to the attractive interaction between the halide and axial hydrogens of the ring.[33] The chelating rings in (L-L)$Mn(CO)_3Br$ remain in chair confromation in solutions.[26]

Thermal or photochemical reaction of *fac*-[(*P,P'*-P_2S)$MnBr(CO)_3$ provided no formation of [*P,P'S*-(tripodal)$Mn(CO)_3]^+$ or [*P,P'*S-(tripodal)$Mn(CO)_2Br$]. The formation of tridentate mode of mixed tripodal ligand in metal complexes was achieved by the treatment of either stereoisomer of *fac*-[(η^2-tripodal)$MnBr(CO)_3$] with silver nitrate, tetrafluoroborate and hexafluorophosphate. Thus

fac-[η^3-(tripodal)Mn(CO)$_3$]$^+$ species **14-16** were obtained.[34] Crystal analysis of [*P,P'*S-(P_2S)Mn(CO)$_3$]$^+$ shows the bond distances of Mn-P and Mn-S and bond angles along all bonds to lie in normal ranges, except that one angle S-Mn-P (80.88°) deviated from normal 90°. Due to the chelation effect, these η^3-complexes exhibit particular thermal stability. [*P,P'S*-(P_2S)Mn(CO)$_3$]PF_6 is stable under refluxing THF or acetonitrlie. No exchange of CO ligand was observed when the complex was exposed to ^{13}CO at atmospheric pressure. Photochemically, **16** underwent ligand substitution of CO by phosphines, such as diphenylphosphine, triethylphosphine and triethylphsophite, to give **17**. Such a complex reacts with halides and psuedoha-lides stereospecifically to give *syn-fac*-[η^2-(tripodal)Mn-(CO)$_3$X], in where tripodal = P_2S, PS_2, P_2O(H); X = Br, I, SCN. The rate law has the form

$$\text{rate} = k_{obs}[(\eta^3\text{-}P_2S)Mn(CO)_3^+][X^-]$$

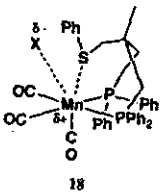
consistent with a second-order reaction. Thus the mechanism of such stereospecificity is believed to proceed through a seven-coordinated species **18** (X = Br, I, SCN).



14, W = SPh
15, W = OH

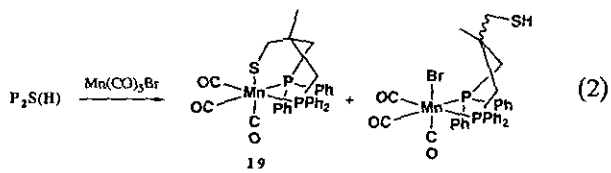
16

17



18

When tripodal P_2S(H) reacts with Mn(CO)$_5$Br a neutral η^3-complex **19** is produced directly, accompanied with [*P,P'*-{P_2S(H)}Mn(CO)$_3$Br] in minor portion (Eq. 2).[21] Complex **19** is inert toward halides even at higher temperature of reaction. Crystal analysis of **19** reveals that the bond distance Mn-S (2.367 Å) is similar to that in **14** (2.380 Å); the charge interaction between incoming ligand and metallic center is important in accelerating the reaction.



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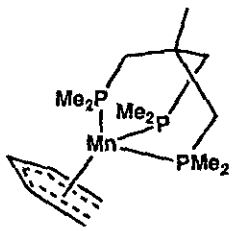
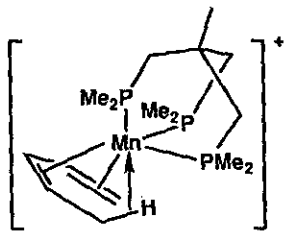
(2)

Besides carbonyl complexes, dienyl manganese(I) complexes were also reported. Reaction of $MnBr_2$ with pentadienide in the presence of P_3(Me) or P_3(Et) would produce (η^5-pentadienyl)Mn[*P,P',P''*-P_3(Me)] **20** or (η^5-pentadienyl)Mn[*P,P',P''*-P_3(Et)].[35] In (η^5-pentadienyl)-Mn[*P,P',P''*-P_3(Et)], the dienyl lignad rotates with respect to the $MnFP_3$ fragment with a barrier of 18.3 kcal/mol. The mechanism of this fluxional behavior involves (a) rearrangement of η^5- to η^3- of dienyl ligand (b) rotation of η^3-ligand (c) conversion of η^3- back to η^5- mode. Interestingly, complex **20** reacted with H^+ to form the protonated species **21**, in which the added proton had an agostic interaction with manganese metal center.[36]



20



21

PROSPECTS

Most work involving tripodal ligands has so far concentrated on the synthesis and coordination chemistry. In future the reactivity of transition metal complexes will be an important subject of research. Stereospecific reaction of [η^3-(tripodal)Mn(CO)$_3$]$^+$ by halides provides significant mechanistic information about ligand substitution and the interaction of C-H-M in **21** accommodates an impotant information conceming the agostic interaction. Although in this account I emphasize phosphine chemistry, the intermediates in syntheses of tripodal ligands, which contain different types of oxygen or nitrogen donors, are potential tripodal ligands for various metallic ions.

ACKNOWLEDGMENT

I would like to thank all my coworkers, whose effort brought this work possible and the National Science Council (ROC) for financial support.

Received September 22, 1992.

Key Words

Tripodal ligands; Phosphines; Manganese(I).

REFERENCES

1. Sacconi, L.; Mani, F. *Transition Met. Chem.* **1982**, *8*, 180.
2. (a) Hewertson, W.; Watson, H. R. *J. Chem. Soc.* **1962**, 1490. (b) Chatt, J.; Hart, F. A. *J. Chem. Soc.* **1960**, 1378.
3. Issleib, K.; Abicht, H. P. *J. Prakt. Chem.* **1970**, *312*, 456.
4. (a) King, R. B.; Kapoor, R. N.; Saran, M. S.; Kapoor, P. N. *Inorg. Chem.* **1971**, *10*, 1851. (b) King, R. B.; Cloyd, J. C. Jr.; Reimann, R. H. *J. Org. Chem.* **1976**, *41*, 972. and references therein.
5. Dyer, G.; Meek, D. W. *Inorg. Chem.* **1965**, *4*, 1398. (b) Dyer, G.; Meek, D. W. *Inorg. Chem.* **1967**, *6*, 149.
6. For those ligands (n = 0 in **I**) are designed as the perfect "bite angle" for three metal atoms. See ref. Rimmelin, J.; Lemoine, P.; Maurice, G.; Bahsoun, A. A.; Osborn, J. A. *Nouv. J. Chim.* **1985**, *9*, 181; Darensbourgh, D. J. Zalewski, D. J. *Organometallics* **1985**, *4*, 92. However, the chemistry of this type of ligands is not discussed here.
7. Brodersen, K.; Rolz, W.; Jordan, G.; Gerbeth, R.; Ellermann, J. *Chem. Ber.* **1978**, *111*, 132.
8. Sabatini, A.; Vacca, A. *Coord. Chem. Rev.* **1975**, *16*, 161.
9. Whiteside, G. M.; Casey, C. P.; Krieger, C. *J. Am. Chem. Soc.* **1971**, *93*, 1379.
10. Berglund, D.; Meek, D. W. *Inorg. Chem.* **1972**, *11*, 1493.
11. Liu, S.-T.; Yieh, C.-H.; Lu, H.-J. *Phosphorus, Sulfur Silicon* **1989**, *44*, 261.
12. Liu, S.-T.; Wang, H.-E.; Cheng, M.-C.; Peng, S.-M. *J. Organomet. Chem.* **1989**, *376*, 333.
13. Wang, H.-E.; Liu, C.-Y.; Cheng, M.-C.; Peng, S.-M.; Liu, S.-M.; Liu, S.-T. *Phosphorus Sulfur Silicon* **1992**, *69*, 201.
14. McAlees, A. J.; McCrindle, R.; Woon-Fat, A. R. *Inorg. Chem.* **1976**, *15*, 1065.
15. Liu, S.-T.; Liu, G.-J. *Inorg. Chem.* **1990**, *29*, 4576.
16. Liu, G.-J. Master's thesis, National Taiwan University, **1989**.
17. Liu, S.-T.; Tsao, C.-L.; Cheng, M.-C.; Peng, S.-M. *Polyhedron* **1990**, *9*, 2579.
18. Liu, S.-T.; Liu, G.-J, unpublished results.
19. Liu, S.-T. The annual report to National Science Council, **1990**.
20. Hsieh, T.-Y. Master's thesis, National Taiwan University, **1989**.
21. Huang, C.-T.; Liu, S.-T., unpublished results.
22. Liu, S.-T.; Liu, C.-Y. *J. Org. Chem.* **1992**, *57*, 6079.
23. (a) Liu, S.-T.; Liu, K.-J.; Yieh, C.-H.; Cheng, M.-C.; Peng, S.-M., *J. Organomet. Chem.* **1990**, *387*, 83. (b) Wang, H.-E.; Liu, S.-T.; Lee, G.-H.; Cheng, M.-C.; Peng, S.-M. *J. Chin. Chem. Soc.* **1991**, *38*, 565. (c) Wang, H.-E.; Cheng, M.-C.; Lee, G.-H.; Peng, S.-M.; Liu, S.-T. *J. Organomet. Chem.* accepted for publication.
24. King, R. B.; Efraty, A. *Inorg. Chem.* **1969**, *8*, 2374.
25. Ellermann, J.; Lindner, H. A. *Z. Naturforsch. B. Anorg., Chem. Org.* **1976**, *31B*, 1350.
26. Liu, S.-T.; Wang, H.-E.; Yiin, C. -M.; Tsai, S.-C.; Liu, G.-J.; Wang, Y.-M.; Cheng, M.-C.; Peng, S.-M., *Organometallics* accepted for publication.
27. Ellermann, J.; Schindler, J. F. *Chem. Ber.* **1976**, *109*, 1095.
28. Ellermann, J.; Lindner, H. A. *Z. Naturforsch. B: Anorg., Chem. Org.* **1976**, *34B*, 799.
29. Ellermann, J.; Lindner, H. A.; Moll, A. *Chem. Ber.* **1979**, *112*, 3441.
30. Wang, H.-E. Ph. D. Dissertation, National Taiwan University, **1991**.
31. Liu, S.-T. unpublished results.
32. Coville, N. J.; Butler, I. S. *J. Organomet. Chem.* **1973**, *57*, 355.
33. (a) Bear, C. A.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1973**, 673. (b) Cullen, W. R.; Einstein, F. W. B.; Pomeroy, R. K.; Vogel, P. L. *Inorg. Chem.* **1975**, *14*, 3017. (c) Cullen, W. R.; Hall, L. D.; Price, J. T., Spendjian, G. Y. *Inorg. Chem.* **1974**, *13*, 2130.
34. Liu, S.-T.; Wang, H.-E.; Yiin, C. -M.; Tsai, S.-C.; Liu, G.-J.; Wang, Y.-M.; Cheng, M.-C.; Peng, S.-M., manuscripts in preparation.
35. Bleeke, J. R.; Stanley, G. G.; Kotyk, J. J. *Organometallics* **1986**, *5*, 1642.
36. Bleeke, J. R.; Kotyk, J. J.; Moore, D. A.; Rauscher, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 417.