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COORDINATING PROPERTIES OF 2-PYRIDYLDIPHENYLPHOSPHINE WITH SOME METAL CARBONYLS

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Abstract—The reaction of 2-pyridyldiphenylphosphine with iron carbonyl affords 2-$(C_5H_4N)P(C_6H_5)_2Fe(CO)_4$ in which the ligand is bonded through the phosphorus donor atom. Similar substitution reactions occur with $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Cr(CO)_6$ and $Mo(CO)_6$ to give 2-$C_5H_4NP(C_6H_5)_2Mn_2(CO)_8$, $[2\text{-}C_5H_4NP(C_6H_5)_2Re(CO)_4]_2$ and 2-$C_5H_4NP(C_6H_5)_2M(CO)_5$ (M = Cr, Mo), respectively.

2-Pyridyldiphenylphosphine (I) has attracted much interest as a ligand[1] especially in the synthesis of bridged heteroatomic transition metal complexes.[2–8] The present study sets out to investigate the coordinating properties of ligand **I** with various transition metal carbonyls under conditions similar to those reported in our earlier studies[9–13] involving the reactivities of (*o*-diphenylphosphinobenzyl)dimethylsilane and 2-pyridyldimethylsilane towards metal carbonyls. We report below the preparation and properties of complexes obtained from reactions of **I** with metal carbonyls of chromium, molybdenum, manganese, rhenium and iron.

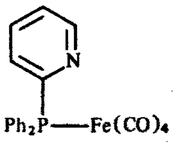
RESULTS AND DISCUSSION

Iron complex

Ligand **I** was prepared in this study by the reaction between the Grignard reagent 2-C_5H_4NMgBr and chlorodiphenyl phosphine in ether:

$$2C_5H_4NMgBr + ClP(C_6H_5)_2 \longrightarrow 2C_5H_4NP(C_6H_5)_2 + MgBrCl.$$

Treatment of the distillate at 120–140°C/0.5 mm Hg gave **I** as a crystalline solid. The reactions of **I** with iron pentacarbonyl in benzene proceeded at 125°C to give a monosubstituted iron carbonyl derivative, $C_5H_4NP(C_6H_5)_2Fe(CO)_4$ (**II**), formulated on the basis of IR data and elemental analysis. The same product was also obtained from the reaction of diiron nonacarbonyl with **I** at 40°C. Prolonged reaction of more than 18 h did not yield the disubstituted derivative. This is to be contrasted with the reaction[13] of *o*-chlorophenyldiphenylphosphine with iron pentacarbonyl and diiron nonacarbonyl wherein a disubstituted complex $[o\text{-}ClC_6H_4P(C_6H_5)_2]_2Fe(CO)_3$ (**A**) was obtained in the former case, while both monosubstituted $o\text{-}ClC_6H_4P(C_6H_5)_2Fe(CO)_4$ (**B**) and the disubstituted **A** derivatives were isolated in the latter. The IR spectra of complexes **A** and **B** display carbonyl stretching vibrations at 1970, 1930, 1890, 1870 cm^{-1} and 2050, 1975, 1946 cm^{-1}, respectively. The carbonyl stretching vibrations of **II** are located at 2050, 1980, 1940 and 1890 cm^{-1}. This suggests that bonding of **I** to iron is most likely to occur through the phosphorus atom only, as shown in structure **II**.



II

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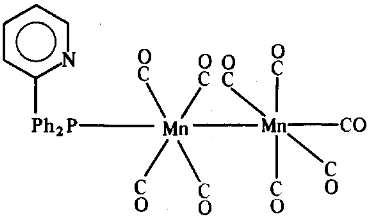
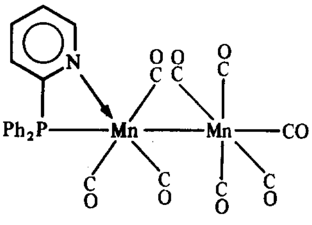
This mode of bonding is consistent with the basic reaction pattern established by Balch and co-workers[3] for formation of bridged heteronuclear-transition metal complexes. The first step invariably led to the formation of the monosubstituted derivative with **I** being bonded to the metal by the phosphorus atom. Moreover, the low affinity[14] of iron(0) for the pyridine nitrogen has been further demonstrated by a reaction of $(C_5H_4N)_2Si(CH_3)_2$ and diiron noncarbonyl in benzene at 100°C, from which only triiron dodecacarbonyl and unreacted ligand were isolated.[13] It is also noted that the pyridine vibrations at 604 and 405 cm^{-1} have not been appreciably affected in compound **II**.[15]

Manganese and rhenium complexes

The reactions of **I** with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ proceeded in benzene at a much higher temperature of 160°C. The manganese derivative **III** is an orange solid characterized by seven CO stretching vibrations at 2060, 2000, 1982, 1960, 1940, 1930 and 1902 cm^{-1}. Its analytical data do not differentiate it between the formula $C_5H_4NP(C_6H_5)_2Mn_2(CO)_9$ (**IIIa**) and $C_5H_4NP(C_6H_5)_2Mn_2(CO)_8$ (**IIIb**). The IR data are not consistent with structure **IIIa** which normally gives five bands.[16] However, the presence of seven bands suggests that the most probable structure is **IIIb**.

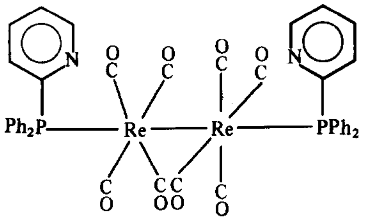


(IIIa)



(IIIb)

The complex formed with the rhenium carbonyl can be formulated as $[2\text{-}C_5H_4NP(C_6H_5)_2Re(CO)_4]_2$ (**IV**) on the basis of elemental analysis and CO stretching vibrations which gave bands located at 2080, 1980, 1940 and 1902 cm^{-1}. Following from the above discussion, structure **IV** is proposed. The lower number of CO stretching vibrations observed in this case is consistent with the high symmetry of structure **IV** compared to the manganese analogue (**IIIb**).



(IV)

Chromium and molybdenum complexes

The reactions between ligand **I** and chromium carbonyl proceeded in benzene at a temperature of 105°C to give a creamy crystalline solid which can be formulated as $C_5H_4NP(C_6H_5)_2Cr(CO)_5$ (**V**) on the basis of its IR data and elemental analysis. An analogous monosubstituted molybdenum(0) derivative (**VI**) was also obtained from a reaction with molybdenum hexacarbonyl at 125°C in benzene. As both chromium and molybdenum form monopyridine[17] as well as monotriphenylphosphine[18] complexes of the general formula $LM(CO)_5$ (L = pyridine/triphenylphosphine), attempts were made to ascertain the mode of coordination of **I** in **V** and **VI**. A careful comparison of the carbonyl stretching frequencies of several complexes (Table 1) reveals that synergic interactions of triphenylphosphine with chromium(0) and molybdenum(0) is apparently greater than with pyridine.

EXPERIMENTAL

The IR spectra of solids, as KBr pellets, were recorded on a Perkin–Elmer Model 337 IR spectrophotometer. The IR spectra of metal carbonyl complexes in the carbonyl region were recorded on chloroform solutions.

Synthesis of 2-pyridyldiphenylphosphine

A solution of ethyl bromide (2.2 g, 0.02 mol) in dry ether (50 cm^3) was added to dry magnesium turnings (15.0 g, 0.62 mol) placed in a three-necked flask. A few iodine crystals were added to initiate the reaction. A solution of 2-bromopyridine (76.9 g, 0.49 mol) and ethyl bromide (24.8 g, 0.23 mol) in ether (250 cm^3) was added over 75 min while keeping the reaction mixture under reflux. After a further reflux for another 2 h, the reaction mixture was cooled. A solution of diphenylchlorophosphine (70.6 g, 0.32 mol) in ether (275 cm^3) was added slowly and the resultant reaction mixture was refluxed for a further 2 h. Upon cooling, the reaction mixture was treated with saturated ammonium chloride solution (275 cm^3). The ether layer was dried over anhydrous sodium sulphate overnight and fractional distillation at 180°C/1–2 mm Hg yielded 2-pyridyldiphenylphosphine (26.9 g), m.p. 84–85°C. (Found: C, 77.5; H, 5.3; N, 5.1. Calc. for $C_{17}H_{14}NP$: C, 77.6; H, 5.3; N, 5.3%.) IR (Nujol mull): 3050w, 2950s, 2920s, 2860s, 1565m, 1460s, 1435s, 1412s, 1090m, 1048m, 1025m, 998m, 772s, 746s, 716m, 695s, 620m.

Reaction of 2-*pyridyldiphenylphosphine with chromium hexacarbonyl*

A mixture of chromium hexacarbonyl (0.50 g, 2.27 mmol), 2-pyridyldiphenylphosphine (0.50 g, 1.90 mmol) and benzene (10 cm^3) was sealed in an evacuated tube and kept at 105°C for 20 h. The solution was then filtered and concentrated to yield a solid. Yellow crystals were obtained upon recrystallization from acetone, $C_5H_4NP(C_6H_5)_2$ $Cr(CO)_5$, m.p. 107–109°C. (Found: C, 58.2; H, 3.3. Calc. for $C_{22}H_{14}CrO_5NP$: C; 58.0; H, 3.1%.) IR ($CHCl_3$ solution): 2060s, 1995m, 1920vs, 1660w, 1570s, 1480w, 1420m, 1320w, 1300w, 1090s, 990s, 630s.

Reaction of 2-*pyridyldiphenylphosphine with molybdenum hexacarbonyl*

A mixture of molybdenum hexacarbonyl (0.56 g, 2.12 mmol), 2-pyridyldiphenylphosphine (0.50 g, 1.90 mmol) and benzene (10 cm^3) was sealed in an evacuated tube at 126°C for 18 h. The solution was then filtered and concentrated to give a solid which upon recrystallization from acetone formed yellow crystals of $C_5H_4NP(C_6H_5)_2Mo(CO)_5$, m.p. 119–121°C. (Found: C, 53.5; H, 3.1. Calc. for $C_{22}H_{14}MoO_5NP$: C, 52.9; H, 2.8%.) IR: 2075s, 1995m, 1940vs, 1710w, 1580s, 1430m, 1329w, 1301w, 1151w, 1090s, 1000sh, 990s, 900m, 608s.

Reaction of 2-*pyridyldiphenylphosphine with manganese carbonyl*

A mixture of 2-pyridyldiphenylphosphine (0.59 g, 2.25 mmol), manganese carbonyl (0.899, 2.28 mmol) and benzene (15 cm^3) was sealed in a tube at 160°C for *ca* 10 min. The solution was filtered and the filtrate concentrated under nitrogen. The orange–brown solid obtained was subjected to vacuum sublimation at 50°C to remove the unreacted parent carbonyl. The residue was then recrystallized from hexane to yield bright orange crystals, m.p. 181–182°C. This compound was identified as 2-$C_5H_4NP(C_6H_5)_2Mn_2(CO)_8$. (Found: C, 50.1; H, 2.6; N, 2.2. Calc. for $C_{25}H_{14}PNMn_2O_8$: C, 49.9; H, 2.2; N, 2.2%.) IR ($CHCl_3$ solution): 2980m, 2060s, 2000m, 1985s, 1960s, 1940s, 1930s, 1902s, 1460m, 1430m, 1180w, 1160w, 1125w, 1095w, 1085w, 1020w, 1000w, 765m, 750m, 720m, 695m, 663s, 645s, 623s.

Reaction of 2-*pyridyldiphenylphosphine with rhenium carbonyl*

A mixture of 2-pyridyldiphenylphosphine (0.263 g, 0.89 mmol), rhenium carbonyl (0.695 g, 1.06 mmol) and benzene (10 cm^3) was sealed in an evacuated tube at 160°C for 2 h. The solvent was removed under vacuum and the residual was subjected to sublimation at 80°C to remove the unreacted rhenium carbonyl. The remaining solid was fractionally recrystallized from hexane to give white crystals, m.p. 219–220°C. This compound was identified as $[2\text{-}C_5H_4NP(C_6H_5)_2Re(CO)_4]_2$. (Found: C, 44.7; H, 2.0; N, 2.1. Calc. for $C_{42}H_{28}P_2N_2Re_2O_8$: C, 44.9; H, 2.5; N, 2.5%.) IR ($CHCl_3$ solution): 3050w, 2940s, 2845s, 2095w, 2060w, 2020sh, 2008m, 1980s, 1940vs, 1902s, 1565m, 1485m, 1420s, 1450s, 1418m, 1375m, 1185w, 1155w, 1095sh, 1078m, 1020w, 1000w, 988w, 765w, 743m, 720w, 698m, 625m, 615s.

Reaction of 2-*pyridyldiphenylphosphine with iron pentacarbonyl*

A mixture of 2-pyridyldiphenylphosphine (0.51 g, 1.92 mmol), iron pentacarbonyl (0.429 g, 2.51 mmol) and benzene (8 cm^3) was placed in a sealed tube at 125°C for 11 h. The resultant solution was filtered and the filtrate concentrated under nitrogen. The yellow crystals formed were recrystallized from acetone. The product (m.p. 155–157°C decomp.) was identified as 2-$C_5H_4NP(C_6H_5)_2Fe(CO)_4$. (Found: C, 59.1; H, 3.5; N, 3.0. Calc. for $C_{21}H_{14}NPFeO_4$: C, 58.5; H, 3.2; N, 3.2%.) IR ($CHCl_3$ solution): 3060w, 3050w, 2940s, 2910s, 2850s, 1995w, 1970s, 1930m, 1890s, 1870s, 1570w, 1480m, 1465m, 1455m, 1435m, 1425s, 1375m, 1365w, 1270w, 1255m, 1180w, 1125w, 1108m, 1095m, 1038m, 995w, 873w, 758s, 738m, 715m, 708m, 695s, 638s.

REFERENCES

1. H. G. Ang, W. E. Kow and K. F. Mok, *Inorg. Nucl. Chem. Lett.* 1972, **8**, 829.
2. M. J. Auburn and F. A. Cotton, *J. Am. Chem. Soc.* 1984, **106**, 1323.

3. J. P. Farr, M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc.* 1980, **102**, 6654.
4. A. Maisonnet, J. P. Farr and A. L. Balch, *Inorg. Chem. Acta* 1981, **53**, L217.
5. J. P. Farr, M. M. Olmstead, C. H. Hunt and A. L. Balch, *Inorg. Chem.* 1981, **20**, 1182.
6. A. Maisonnet, J. P. Farr, M. M. Olmstead, C. T. Hunt and A. L. Balch, *Inorg. Chem.* 1982, **21**, 3961.
7. J. P. Farr, M. M. Olmstead and A. L. Balch, *Inorg. Chem.* 1983, **22**, 1229.
8. J. P. Farr, M. M. Olmstead, F. E. Wood and A. L. Balch, *J. Am. Chem. Soc.* 1983, **105**, 792.
9. H. G. Ang and P. T. Lau, *J. Organomet. Chem.* 1985, **291**, 285.
10. H. G. Ang and P. T. Lau, *J. Organomet. Chem.* 1972, **37**, C4.
11. H. G. Ang and P. T. Lau, *Organometallic Chem. Rev. A* 1972, **8**, 235.
12. H. G. Ang and W. L. Kwik, *J. Organomet. Chem.* 1989, **361**, 27.
13. H. G. Ang, unpublished results.
14. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn. John Wiley, New York (1988).
15. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn. John Wiley, New York (1986).
16. R. H. Reimann and E. Singleton, *J. Chem. Soc., Dalton Trans.* 1976, 2109.
17. C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.* 1963, **2**, 533.
18. T. A. Magel, C. N. Matthews, T. S. Wang and J. H. Wotiz, *J. Am. Chem. Soc.* 1961, **83**, 3200.