# Aminocyclophosphazene Derivatives of Tungsten Carbonyl

A. K. Shrimal

Chemistry Department, University of Gorakhpur, Gorakhpur - 273009, India

Reprint requests to Dr. A. K. Shrimal

Z. Naturforsch. 54 b, 1543–1546 (1999); received August 19, 1999

Aminocyclophosphazene Derivatives, Tungsten Carbonyl

Reactions of aminated cyclotri- and cyclotetra-phosphazenes, viz,  $N_3P_3L_6$  and  $N_4P_4L_8$ (L = -NC<sub>4</sub>H<sub>8</sub>O, -NC<sub>5</sub>H<sub>10</sub>, -HNC<sub>6</sub>H<sub>11</sub> and -HNC<sub>8</sub>H<sub>17</sub>) with W(CO)<sub>6</sub> have been studied. [(N<sub>3</sub>P<sub>3</sub>L<sub>6</sub>)W(CO)<sub>3</sub>] derivatives are obtained with N<sub>3</sub>P<sub>3</sub>L<sub>6</sub> while N<sub>4</sub>P<sub>4</sub>L<sub>8</sub> yield tetracarbonyl substituted derivatives, [(N<sub>4</sub>P<sub>4</sub>L<sub>8</sub>)W(CO)<sub>4</sub>]. Mixed ligand tungsten tricarbonyls of the type [C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)(N<sub>3</sub>P<sub>3</sub>L<sub>6</sub> or N<sub>4</sub>P<sub>4</sub>L<sub>8</sub>)W(CO)<sub>3</sub>] have also been synthesized with [(*o*-phen)W(CO)<sub>4</sub>].

# Introduction

Preliminary reports [1,2] based on spectroscopic data indicated that halophosphazenes,  $N_3P_3X_6$  and  $N_4P_4X_8$  (X=Cl, Br) do not form complexes by reacting with transition metal halides. Cyclophosphazenes with alkyl, -HNR, -NR<sub>2</sub> substituted phosphorus are more basic than the halides as expected on the basis of their pKa values. Such complexes of cyclophosphazenes were first reported [3] in 1966 but without detailed structural informations. Since then considerable studies [4 - 7] have been done on the reactions of cyclophosphazenes with transition metal ions, but these donors have not been exploited to an appreciable extent in the CO displacements of metal carbonyls [8 - 13].

In order to study the contribution of exocyclic nitrogen atoms, the ring nitrogen atoms or the cyclophosphazene nucleus itself to the coordination of metal carbonyl moieties, the reactions of several aminocyclophosphazenes,  $N_3P_3L_6$  and  $N_4P_4L_8$  (L = -NC<sub>4</sub>H<sub>8</sub>O, -NC<sub>5</sub>H<sub>10</sub>, -HNC<sub>6</sub>H<sub>11</sub> and -HNC<sub>8</sub>H<sub>17</sub>) with hexacarbonyltungsten(0) and (*o*-phenanthroline)tetracarbonyltungsten(0) have been studied in the present paper.

## Experimental

 $N_3P_3Cl_6$  and  $N_4P_4Cl_8$  were first synthesized by the reaction of finely divided  $NH_4Cl$  and  $PCl_5$  in refluxing *sym.*tetrachloroethane. After separating the linear and cyclic polymers, cyclophosphazenes were separated by standard procedures [14] which involve fractional crystallization with the help of glacial acetic acid, cold benzene and conc.  $H_2SO_4$ . Trimers and tetramers were identified by their m.ps. and mass spectra. Aminocyclophosphazenes were then synthesized by reacting  $N_3P_3Cl_6$  or  $N_4P_4Cl_8$  with appropriate amines. The aminocyclophosphazenes were characterized by comparing their m.ps. with literature data [15 - 18].

(*o*-Phenanthroline)tetracarbonyltungsten(0) was prepared by the method given in lit. [19]. Hexacarbonyltungsten(0) was purchased from Strem Chemicals, Inc., U.S.A.

IR spectra were recorded on a Perkin-Elmer (model-557) spectrophotometer in KBr discs.

*Preparation of (hexamorpholinocyclotriphosphazene)tricarbonyltungsten(0)* 

Hexacarbonyltungsten(0) (0.20 g) and hexamorpholinocyclotriphosphazene (0.37 g) were refluxed together for 10 h in xylene (20 ml) under argon atmosphere. A yellow compound was obtained on cooling the reaction mixture and removing the solvent *in vacuo*. Unreacted hexacarbonyltungsten(0) was removed by sublimation and the product was extracted with hexane to leave the unreacted phosphazene. The hexane extract was dried *in vacuo* to give the yellow product which was recrystallized from benzene. Yield 66.2 %.

C<sub>27</sub>H<sub>48</sub>N<sub>9</sub>O<sub>9</sub>P<sub>3</sub>W (918.85) Calcd C 35.25 H 5.22 N 13.71 P 10.12 %, Found C 35.80 H 5.31 N 13.84 P 10.18 %.

## *Preparation of (octamorpholinocyclotetraphosphazene)tetracarbonyltungsten(0)*

Hexacarbonyltungsten(0) (0.20 g) and octamorpholinocyclotetraphosphazene (0.49 g) were refluxed together for 6 h in xylene (20 ml) under argon atmosphere. A yellow compound was obtained by cooling the reaction mixture and removing the solvent *in vacuo*. Unreacted parent carbonyl was removed by sublimation

Κ

0932–0776/99/1200–1543 \$ 06.00 © 1999 Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com

| Complex   | Solvent/ Colour Yield (%) Found (Calcd) (%) |        |          | )       |         |         |         |
|---|---|--------|----------|---------|---------|---------|---------|
|   | reaction time (h)                           |        |          | С       | H       | N       | Р       |
| $[\{N_3P_3(C_5H_{10}N)_6\}W(CO)_3]$   | xylene/12                                   | yellow | 52.5     | 43.48   | 6.64    | 13.82   | 10.18   |
|   |   |        | (2.4     | (43.66) | (6.62)  | (13.89) | (10.25) |
| $[\{N_3P_3(C_6H_{11}NH)_6\}W(CO)_3]$  | xylene/10                                   | yenow  | 62.4     | (47.12) | (10.84) | (12.08) | (9.32)  |
| $[{N_3P_3(C_8H_{17}NH)_6}W(CO)_3]$  | xylene/6                                    | yellow | 58.2     | 52.34   | 9.20    | 10.72   | 7.88    |
|   | -   |        |          | (52.26) | (9.22)  | (10.76) | (7.94)  |
| $[{N_4P_4 (C_5H_{10}N)_8}W(CO)_4]$  | xylene/8                                    | yellow | 56.2     | 45.88   | 6.94    | 14.61   | 10.72   |
|   |   |        |          | (45.99) | (6.97)  | (14.63) | (10.80) |
| $[\{N_4P_4(C_6H_{11}NH)_8\}W(CO)_4]$  | xylene/4                                    | yellow | 58.6     | 49.48   | 11.36   | 13.24   | 9.82    |
|   |   |        |          | (49.52) | (11.43) | (13.33) | (9.84)  |
| $[\{N_4P_4(C_8H_{17}NH)_8\}W(CO)_4]$  | xylene/3                                    | yellow | 59.4     | 54.48   | 9.54    | 11.26   | 8.18    |
|   |   |        |          | (54.40) | (9.60)  | (11.20) | (8.26)  |
| $[(C_{12}H_8N_2) \{N_3P_3(C_5H_{10}N)_6\}W(CO)_3]$                                      | xylene/24                                   | black  | 48.8     | 49.62   | 6.30    | 14.20   | 8.52    |
|   |   |        | <b>-</b> | (49.68) | (6.25)  | (14.17) | (8.55)  |
| $[(C_{12}H_8N_2)\{N_3P_3(C_6H_{11}NH)_6\}W(CO)_3]$                                      | xylene/18                                   | black  | 51.4     | 52.20   | 6.85    | 13.22   | 7.92    |
|   | 1 /1/                                       |        | 16.0     | (52.26) | (6.83)  | (13.15) | (7.94)  |
| $[(C_{12}H_8N_2)\{N_3P_3(C_8H_{17}NH)_6\}W(CO)_3]$                                      | xylene/16                                   | black  | 46.2     | 55.88   | 8.52    | 11.36   | 6.42    |
|   | 1 /01                                       | 11.1   | 516      | (55.95) | (8.59)  | (11.40) | (0.88)  |
| $[(C_{12}H_8N_2)\{N_4P_4(C_5H_{10}N)_8\}W(CO)_3]$                                       | xylene/21                                   | black  | 54.6     | 50.75   | 0.70    | 15.14   | 9.52    |
| $\left[\left(C, H, N\right)\left(N, P, \left(C, H, NO\right)\right)\right]$             | ····1 ··· · /1 9                            | blash  | 500      | (50.77) | (0.77)  | (15.08) | (9.54)  |
| $[(C_{12}H_8N_2){N_4P_4(C_4H_8NO)_8} w(CO)_3]$  | xylene/18                                   | DIACK  | 38.8     | 42.72   | 5.48    | 14.82   | 9.38    |
| [(C, U, N) (N, D, (C, U, NU))] W(CO)]   | wylana/16                                   | blash  | 62.2     | (42.79) | (3.40)  | (14.87) | (9.42)  |
| $[(C_{12}\Pi_8 \Pi_2) \{ \Pi_4 P_4 (C_6 \Pi_{11} \Pi_1 \Pi_1)_8 \} W (CO)_3 ]$          | xylene/16                                   | DIACK  | 02.2     | (52.54) | (7.36)  | (12.00) | 9.44    |
| $[(C_{1}H_{1}N_{2})] \times [(C_{2}H_{1}NH_{2})] \times [(C_{2}H_{2}NH_{2})]$           | vylana/15                                   | black  | 10.8     | (33.34) | 0.32    | (13.00) | 7.49    |
| $[(C_{12}, 1_{8}, 1_{2}) \{ 1_{4}, 1_{4}, (C_{8}, 1_{1}, 1_{1}, 1_{1}) \} W (CO)_{3} ]$ | xyielle/15                                  | UTACK  | 47.0     | (57.32) | 9.52    | (11.70) | (7.51)  |
|   |   |        |          | (57.50) | (9.20)  | (11.00) | (7.51)  |

Table I. Preparative conditions, colour and analysis of complexes.

Table II. CO Stretching frequencies of complexes.

| Complex  | Frequency (mode) (cm <sup>-1</sup> )   |
|--|--|
| $[{N_3P_3(C_5H_{10}N)_6}W(CO)_3]$                  | 1970 s (A <sub>1</sub> ), 1885 s (E)   |
| $[{N_3P_3(C_4H_8NO)_6}W(CO)_3]$                    | 1975 s (A <sub>1</sub> ), 1886 s (E)   |
| $[{N_3P_3(C_6H_{11}NH)_6}W(CO)_3]$                 | 1972 s (A <sub>1</sub> ), 1884 s (E)   |
| $[{N_3P_3(C_8H_{17}NH)_6}W(CO)_3]$                 | 1970 s (A <sub>1</sub> ), 1880 s (E)   |
| $[{N_4P_4 (C_5H_{10}N)_8}W(CO)_4]$                 | 1995 sh $(A_1^{-1})$ , 1930 s $(A_1^{-2})$ , 1850 s $(B_1)$ 1820 w $(B_2)$   |
| $[{N_4P_4(C_4H_8NO)_8}W(CO)_4]$                    | 1985 w $(A_1^{-1})$ , 1935 s $(A_1^{-2})$ , 1845 s $(B_1)$ , 1825 sh $(B_2)$ |
| $[{N_4P_4(C_6H_{11}NH)_8}W(CO)_4]$                 | 1990 sh $(A_1^2)$ , 1925 s $(A_1^2)$ , 1842 s $(B_1)$ , 1812 w $(B_2)$       |
| $[{N_4P_4(C_8H_{17}NH)_8}W(CO)_4]$                 | 1988 $sh(A_1^{-1})$ , 1932 $s(A_1^{-2})$ , 1854 $s(B_1)$ 1818 $w(B_2)$       |
| $[(C_{12}H_8N_2) \{N_3P_3(C_5H_{10}N)_6\}W(CO)_3]$ | 1905 s (A'), 1778 s (A"), 1750 s (A')  |
| $[(C_{12}H_8N_2) \{N_3P_3(C_4H_8NO)_6\}W(CO)_3]$   | 1910 s (A'), 1780 s (A"), 1755 s (A')  |
| $[(C_{12}H_8N_2){N_3P_3(C_6H_{11}NH)_6}W(CO)_3]$   | 1908 s (A'), 1790 s (A"), 1760 s (A')  |
| $[(C_{12}H_8N_2){N_3P_3(C_8H_{17}NH)_6}W(CO)_3]$   | 1915 s (A'), 1785 s (A"), 1765 s A')   |
| $[(C_{12}H_8N_2)\{N_4P_4(C_5H_{10}N)_8\}W(CO)_3]$  | 1906 s (A'), 1784 s (A''), 1752 s (A')                                       |
| $[(C_{12}H_8N_2)\{N_4P_4(C_4H_8NO)_8\}W(CO)_3]$    | 1910 s (A'), 1790 s (A"), 1755 s (A')  |
| $[(C_{12}H_8N_2)\{N_4P_4(C_6H_{11}NH)_8\}W(CO)_3]$ | 1912 s (A'), 1780 s (A''), 1760 s (A')                                       |
| $[(C_{12}H_8N_2)\{N_4P_4(C_8H_{17}NH)_8\}W(CO)_3]$ | 1915 s (A'), 1785 s (A"), 1750 s (A')  |

and the remaining product was dissolved in a minimum amount of diethylether. Addition of an excess of hex-

ane to the ether solution caused precipitation of traces of unreacted phosphazene which were removed by filtra-

tion. The supernatant solution was dried *in vacuo* to give the yellow product which was recrystallized in benzene. Yield 52.4 %.

 $\begin{array}{c} C_{36}H_{64}N_{12}O_{12}P_4W~(1164.48)\\ Calcd \ C ~37.11 \ H ~5.50 \ N ~14.43 \ P ~10.05 \ \%,\\ Found \ C ~37.14 \ H ~5.52 \ N ~14.40 \ P ~10.62 \ \%. \end{array}$ 

### Preparation of (o-phenanthroline)(hexamorpholinocyclotriphosphazene)tricarbonyltungsten(0)

(*o*-Phenanthroline)tetracarbonyltungsten(0) (0.20 g) and hexamorpholinocyclotriphosphazene (0.27 g) were refluxed for 20 h in xylene under argon atmosphere during which the mixture turned violet and a black solid began to separate. The solid was filtered off and washed with benzene to remove unreacted ligand and (*o*-phenanthroline)tetracarbonyltungsten(0). The black product was dried *in vacuo*. Yield 52.2 %.

C<sub>39</sub>H<sub>56</sub>N<sub>11</sub>O<sub>9</sub>P<sub>3</sub>W (1099.50) Calcd C 42.58 H 5.09 N 14.01 P 8.46 %, Found C 42.62 H 5.02 N 13.98 P 8.42 %. Other derivatives prepared are given in Table I.

# **Results and Discussion**

 $N_3P_3L_6$  and  $N_4P_4L_8$  react with  $W(CO)_6$  in boiling xylene under argon to give products of different compositions.  $N_3P_3L_6$  displaces three carbonyl groups while  $N_4P_4L_8$  displaces two carbonyl groups from  $W(CO)_6$ . The reactivity order of cyclophosphazene ligands is:

 $-HNC_8H_{17} > -HNC_6H_{11} > -NC_4H_8O > -NC_5H_{10}.$ 

All  $[(N_3P_3L_6)W(CO)_3]$  derivatives are yellow crystalline solids soluble both in polar and nonpolar organic solvents and are fairly stable both in solid state as well as in solution. The IR spectra exhibit two strong CO stretching bands in the region 1970-1975 and 1880-1886 cm<sup>-1</sup> (Table II). The CO bands of these derivatives appear in much higher regions than those of tricarbonyl derivatives containing nitrogen donor ligands in which the metal-nitrogen  $\sigma$ -links have been inferred [20], *e.g.*, [(C<sub>6</sub>H<sub>11</sub>NH<sub>2</sub>)<sub>3</sub>W(CO)<sub>3</sub>],  $\nu$ CO: 1874s, 1718s cm<sup>-1</sup> and [(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>W(CO)<sub>3</sub>],  $\nu$ CO: 1887s, 1724s cm<sup>-1</sup>. Hence, involvement of exocyclic nitrogen atoms in bonding can also be ruled out. The IR spectra of these derivatives in the CO region exhibit a close resemblance [21] to the spectra of (arene)tricarbonyltungsten(0) derivatives. So, it seems that the  $\pi$ -contribution of the ring plays an important role in the case of the [(N<sub>3</sub>P<sub>3</sub>L<sub>6</sub>)W(CO)<sub>3</sub>] derivatives as was predicted on the basis of M.O. theory by Brown [22] in 1966. The CO stretching modes may be assigned as A<sub>1</sub>+E in agreement with the C<sub>3V</sub> local symmetry of the W(CO)<sub>3</sub> moiety.

 $N_4P_4L_8$  react with W(CO)<sub>6</sub> to give *cis*-[( $N_4P_4L_8$ )W(CO)<sub>4</sub>] derivatives when refluxed in xylene for 3-8 h under argon. The IR spectra of these derivatives exhibit four CO stretching bands in the ranges 1985-1995, 1925-1935, 1842-1854 and 1812-1825 cm<sup>-1</sup> (Table II) attributable to  $2A_1+B_1+B_2$  modes of  $C_{2V}$  symmetry. The spectra of these derivatives closely resemble [12] the spectra of [{ $N_4P_4(NMe_2)_8$ }W(CO)\_4], ( $\nu$ CO: 1994, 1928, 1838, 1809 cm<sup>-1</sup>) for which an X-ray study [10] is available. Hence, it is believed that these derivatives also have one ring nitrogen and one exocyclic nitrogen as the donor sites analogous to [ $N_4P_4(NMe_2)_8$ }W(CO)\_4].

The mixed ligand derivatives  $[(N_3P_3L_6 \text{ or } N_4P_4L_8)(o\text{-phen})W(CO)_3]$  were prepared by protracted reflux in xylene for 16-24 h under argon. These derivatives are black crystalline solids, insoluble in hydrocarbons and light petroleum but soluble in methanol to give violet solution. The aminated phosphazenes act as monodentate ligands by donation through exocyclic nitrogen rather than by the ring nitrogen atoms or the ring itself, as inferred on the basis of the IR spectra. Their IR spectra show three strong CO stretching bands in the ranges 1900-1915, 1778-1790 and 1750-1765 cm<sup>-1</sup>. These bands show a close resemblance to the reported [20] structurally similar [(*o*-phen)(amine)W(CO)<sub>3</sub>] derivatives.

#### Acknowledgement

The financial support from University Grants Commission, New Delhi, is thankfully acknowledged. The author is thankful to the Head of the Department of Chemistry, University of Gorakhpur, for providing necessary laboratory facilities.

 B. Lakatos, J. H. Bohus, H. Arpael, Magyar Kem. Foly. 67, 374 (1961). [2] T. Moeller, S. G. Kokalis, J. Inorg. Nucl. Chem. 25, 875 (1963).

- [3] M. F. Lappert, G. Srivastava, J. Chem. Soc. (A) 210 (1966).
- [4] T. Lubben, M. Witt, H. W. Roesky, M. Noltemeyer, H. G. Schmidt, Inorg. Chem. 34, 4275 (1995).
- [5] R. A. Saraceno, G. H. Riding, H. R. Allcock, A. G. Ewing, J. Am. Chem. Soc. **110**, 980 (1988).
- [6] B. P. Baranwal, S. S. Das, Poonam Singh, Z. Naturforsch. 52b, 1039 (1997).
- [7] S. S. Krishnamurthy, Proc. Ind. Acad. Sci. Chem. Sci. 108, 111 (1996) (Ref. cited there in).
- [8] J. Dyson, N. L. Paddock, Chem. Commun. 191 (1966).
- [9] N. L. Paddock, T. N. Rangnathan, J. N. Wingfield, J. Chem. Soc. Dalton Trans. 1578 (1972).
- [10] H. P. Calhoun, N. L. Paddock, J. Trotter, J. Chem. Soc. Dalton Trans. 2708 (1973).
- [11] H. R. Allcock, P. P. Greigger, L. J. Wagner, M. Y. Bernheim, Inorg. Chem. 20, 716 (1981).
- [12] S. C. Srivastava, A. K. Shrimal, R. V. Pandey, Transition Met. Chem. 12, 421 (1987).

- [13] M. A. Beckett, Organomet. Chem. 21, 180 (1992) (Ref. cited there in).
- [14] H. R. Allcock, "Phosphorus Nitrogen Compounds", Academic Press, New York (1972).
- [15] S. K. Ray, R. A. Shaw, J. Chem. Soc. 872 (1961).
- [16] R. Keat, R. A. Shaw, J. Chem. Soc. (A) 908 (1966).
- [17] K. John, T. Moeller, L. F. Audrieth, J. Am. Chem. Soc. 83, 2608 (1961).
- [18] H. R. Allcock, T. J. Fuller, K. Matsumura, Inorg. Chem. 21, 515 (1982).
- [19] W. Hieber, F. Mühlbauer, Z. Anorg. Allg. Chem. 221, 337 (1935).
- [20] S. C. Tripathi, S. C. Srivastava, G. Prasad, A. K. Shrimal, J. Ind. Chem. Soc. LI, 220 (1974).
- [21] H. P. Fritz, J. Manchot, Spectrochim. Acta. 18, 171 (1962).
- [22] D. A. Brown, Transition Metal Chemistry, Marcel Dekker, New York (1966).