Stereoselective Synthesis of 1,5,9-Triphosphacyclododecane and Tertiary Derivatives

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Selective oxidation of $Mo(CO)_3$ complexes of tritertiary 1,5,9-triphosphacyclododecane macrocycles (R_3L) by halogens (X_2 = Cl_2, Br_2, I_2) to Mo(II) triphospha macrocycle complexes of the type $(R_3L)Mo(CO)_2X_2$ [R = $(CH_3)_2CH$ (**2**), $(CH_3)_3SiCH_2$ (**3**), C_2H_5 (**4**), $(CH_3)_2CHCH_2$ (**5**)] allows the high yield and stereoselective liberation of the corresponding tritertiary macrocycles [*syn,syn*-R_3L, R = $(CH_3)_2CH$ (**6**), $(CH_3)_3SiCH_2$ (**7**), C_2H_5 (**8**), $(CH_3)_2$-$CHCH_2$ (**9**)] in good yield (75−80%) by digestion in strong base. This method fails for the parent trisecondary macrocycle (H_3L) and also for the intermediate Mo(II) salts, $[(R_3L)Mo(CO)_3X]A^-$ [X = halide, A^- = halide, BPh_4 (**1**)]. Addition of halogen to $(H_3L)Cr(CO)_3$ gives rise to the new blue-violet complexes $(H_3L)Cr(CO)_2X_2$ [X = Cl_2 (**11**), Br_2 (**12**)]. Paramagnetic susceptibilities indicate that **11** and **12** are low-spin d^4 six coordinate dicarbonyl halo−halide complexes of the type $[(H_3L)Cr(CO)_2X]X$. In this case, the trisecondary 1,5,9-triphosphacyclododecane (H_3L, **13**) may be liberated stereoselectively and in reasonable yield (60−70%) from **11** or **12**. The macrocycles may alternatively be liberated from the Mo(II) dihalo complexes by action of CN^-. The free trisecondary macrocycle can be alkylated nonstereoselectively to give the tritertiary macrocycles [*syn,-anti*-R_3L; R = CH_3 (**24**), C_2H_5 (**8b**), $(CH_3)_3C$ (**25**)]. The inversion of phosphorus in the *syn,syn* isomer **8** to its *syn,anti* analogue, **8b**, was shown to be slow at 156 °C. Exhaustive oxidation of the Mo(0) macrocycle complexes with H_2O_2 or O_3 results in liberation of the corresponding macrocycle trioxides in good yield. All free macrocycles (and oxides) have been characterized by spectroscopic methods and as the hydrochlorides for selected ligands.

Introduction

Linear, acyclic triphosphines have long been known as ligands in transition metal coordination compounds, and we have recently reported studies on acyclic anionic tridentate ligands.[1] Although new reactivity and coordination behavior may be observed and the versatility in coordination behavior available to such ligands is of value in the design of kinetically labile complexes and in the stabilization of reaction intermediates, it also complicates the study of their complexes. In order to restrict this versatility, applications of macrocyclic triphosphines will be of value. The study of complexes of triphosphorus macrocycles will be of interest for a variety of reasons including their similarities to the cyclopentadienyl family of ligands in so far as they will also be $6e^-$ ligands with the ability to occupy three mutually *cis* coordination sites. With the possible exception of high coordination numbers, remaining coordination sites will correspondingly be forced into a mutually *cis* orientation; a situation that may be advantageous in applications of the complexes, *e.g.* in homogeneous catalysis. Their preference for facially capping coordination modes will no doubt also influence other properties such as oxidation/reduction potentials. Since they are neutral and may allow access to lower oxidation states, their complexes should also present interesting deviations in chemical properties from those of cyclopentadienyl and related complexes. The macrocyclic coordination effect may enable stabilization of otherwise excessively labile complexes of mono- or multidentate acyclic phosphines and thus broaden the range of tertiary phosphine complexes that may be studied.

Triphosphorus macrocycle complexes are very rare due to the lack of suitable ligands; the only class of which that have been prepared in the uncoordinated state are those reported by Kyba[2] which were prepared from 1,2-diphosphinobenzene, each phosphorus of which was then coupled to a third donor *via* alkylene bridges under high dilution conditions (Figure 1a). Although this route is general for a range of derivatives based on variations in the alkylene bridges and in the nature of the substituents on the phosphorus atoms, it is not stereospecific, and since the two phosphorus atoms of the diphosphinobenzene unit are chiral in the product, a mixture of stereoisomers is routinely formed. Whereas inversion at nitrogen is relatively facile and the formation of nitrogen macrocycle complexes is generally readily achieved from isomeric ligand mixtures prepared by high dilution methods, barriers to inversion at phosphorus are relatively high and, for a series of chiral trialkyl and dialkylphenyl phosphines, have been reported to lie in the

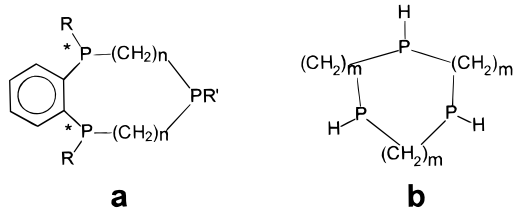

Figure 1. Structures of known macrocyclic triphosphines. n = 2, 3; m = 3, 4; R, R′ = alkyl, aryl.

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Table 1. NMR[a] (ppm) and Mass Spectroscopic Data (*m*/*z*) for Triphosphacyclododecanes

compound	$^{31}P\{^1H\}$[b]	^1H[c]	$^{13}C\{^1H\}$[c]	mass spec
cyclo-$(Me_2CHPC_3H_6)_3$, $^iPr_3L$(**6**)	−19.8 (s)	1.74 (br m) PCH_2	25.7 (dd, $^1J_{PC}$ = 17 Hz, $^3J_{PC}$ = 8 Hz) PCH_2	349 (M^+, 9%)
		1.56 (7 line m) PCH	24.3 (d, $^1J_{PC}$ = 8 Hz) PCH	305 (M − $(C_3H_7)^+$, 38%)
		1.42 (br m) P CH_2CH_2	19.6 (s) CH_3	263 (M − $(C_3H_7)_2^+$, 35%)
		0.99 (dd, $^3J_{PH}$, $^1J_{HH}$ = 15 and 7 Hz) CH_3	19.4 (br s) PCH_2CH_2	219 (M − $(C_3H_7)_3^+$, 27%)
				103 $(P(CH_2)_3P$, 100%)
cyclo-$(Me_3SiCH_2PC_3H_6)_3$, $TMSM_3L$ (**7**)	−43.1 (s)	1.71 (6 line m) PCH_2	30.2 (dd, $^1J_{PC}$ = 17 Hz, $^3J_{PC}$ = 9 Hz) PCH_2CH_2	480 (M^+, 40%)
		1.41 (cm) P CH_2CH_2	19.1 (t, $^2J_{PC}$ = 6 Hz) PCH_2CH_2	393 (M − $(Me_3SiCH_2)^+$, 20%)
		0.56 (d, $^2J_{PH}$ = 2.1 Hz) $SiCH_2$	13.4 (d, $^1J_{PC}$ = 29 Hz) $SiCH_2$	306 (M − $(Me_3SiCH_2)_2^+$, 15%)
		0.80 (s) $SiCH_3$	0.8 (s) $SiCH_3$	
cyclo-$(C_2H_5PC_3H_6)_3$, Et_3L (**8**)	−31.7 (s)	1.72 (7 line m) PCH_2CH_2	27.7 (dd, $^1J_{PC}$ = 16 Hz, $^3J_{PC}$ = 10 Hz) PCH_2CH_2	306 (M^+, 8%)
		1.52 (7 line m) PCH_2CH_3	19.2 (m) PCH_2CH_2	293 (M − CH_2^+, 20%)
		1.36 (7 line m) PCH_2CH_2	19.0 (d, $^2J_{PC}$ = 8 Hz) PCH_2CH_3	277 (M − $C_2H_5^+$, 100%)
		1.02 (dt, $^3J_{PH}$ = 16 Hz, $^2J_{HH}$ 8 Hz) PCH_2CH_3	10.1 (d, $^1J_{PC}$ = 14 Hz) PCH_2CH_3	
cyclo-$(C_2H_5PC_3H_6)_3$, Et_3L_b (**8b**)	−29.4 (t)	1.77 (m) PCH_2CH_2	27.6 (m) PCH_2CH_2	306 (M^+, 22%)
	−38.7 (d)	1.49 (m) PCH_2CH_3	19.2 (m) PCH_2CH_2	277 (M − $C_2H_5^+$, 60%)
	$^4J_{PP}$ = 37 Hz	1.34 (m) PCH_2CH_2	19.0 (d, $^2J_{PC}$ = 10 Hz) PCH_2CH_3	219 (M − $(C_2H_5)_2^+$, 80%)
		1.06 (m) PCH_2CH_3	10.0 (d, $^1J_{PC}$ = 16 Hz) PCH_2CH_3	
cyclo-$(Me_2CHCH_2PC_3H_6)_3$, $^iBu_3L$ (**9**)	−40.8 (s)	1.70 (7 line m) PCH_2CH_2	37.0 (d, $^1J_{PC}$ = 12 Hz) PCH_2CH	391 (M^+, 15%)
		1.52 (7 line m) PCH_2CH	27.5 (dd, $^1J_{PC}$ = 16 Hz, $^3J_{PC}$ = 9 Hz) PCH_2CH_2	350 (M − $C_3H_7^+$, 65%)
		1.37 (7 line m) PCH_2CH_2	26.3 (d, $^2J_{PC}$ = 9 Hz) PCH_2CH	333 (M − $C_4H_9^+$, 100%)
		1.27 (dd, $^2J_{PH}$ = 7 Hz, $^2J_{HH}$ = 3 Hz) PCH_2CH	24.3 (d, $^3J_{PC}$ = 9 Hz) CH_3	277 (M − $(C_4H_9)_2^+$, 20%)
		0.95 (d, $^2J_{HH}$ = 3 Hz) CH_3	19.2 (t, $^2J_{PC}$ = 7 Hz) PCH_2CH_2	219 (M − $(C_4H_9)_3^+$, 20%)
cyclo-$(HPC_3H_6)_3$, H_3L (**13**)	−83.4 (s)[d]	2.89 (m) PH_2	24.4 (br m) PCH_2CH_2	222 (M^+, 60%)
		1.85 (m) PCH_2	18.8 (dd, $^1J_{PC}$ = 11 Hz, $^3J_{PC}$ = 7 Hz) PCH_2	
		1.65 (m) PCH_2CH_2		
cyclo-$(MePC_3H_6)_3$, Me_3L (**24**)	−38.3 (t)	1.82 (m) PCH_2	25.5 (br m) PCH_2	264 (M^+, 5%)
	−49.5 (d)	1.63 (m) PCH_2CH_2	18.9 (br m) PCH_2CH_2	249 (M − CH_3^+, 20%)
	$^4J_{PP}$ = 39 Hz	0.98 (br s) PCH_3	8.6 (d, $^1J_{PC}$ = 16 Hz) PCH_3	234 (M − $(CH_3)_2^+$, 8%)
				219 (M − $(CH_3)_3^+$, 100%)
cyclo-$(Me_3CPC_3H_6)_3$, $^tBu_3L$(**25**)	−9.9 (t)	1.79 (br m) PCH_2CH_2	28.7 (m) PCH_2	390 (M^+, 8%)
	−15.7 (d)	1.56 (m) PCH_2CH_2	24.6 (d, $^1J_{PC}$ = 18 Hz) PC	333 (M − $C(CH_3)_3^+$, 10%)
	$^4J_{PP}$ = 40 Hz	0.98 (br s) CH_3	22.8 (m) PCH_2CH_2	276 (M − $2C(CH_3)_3^+$, 20%)
			13.9 (d, $^2J_{PC}$ = 7 Hz) CH_3	219 (M − $3C(CH_3)_3^+$, 60%)

[a] In $CDCl_3$ solution. [b] Referenced relative to external 85% H_3PO_4 (δ = 0 ppm). [c] Referenced relative to solvent. [d] ^{31}P NMR δ −83.4 (d, $^1J_{PH}$ 203 Hz).

range $\Delta G^{\ddagger}$ = 124−149 kJ mol^{-1}.[3] The presence of stereoisomers clearly complicates the study of the coordination chemistry of these macrocycles, especially since their separation is not generally trivial and results in poor yields of pure individual isomers. For this reason we have investigated routes to symmetrical tridentate macrocyclic ligands (*i.e.* as in Figure 1b with identical bridging backbone functions and hence achiral phosphorus atoms).

The only examples of such macrocycles are in the Mo tricarbonyl complexes of 1,5,9-triphosphacyclododecane and 1,6,11-triphosphacyclopentadecane, both of which were prepared by Norman[4] by the template cyclization of allyl- or 3-butenylphosphine respectively in tris(primary phosphine)molybdenum tricarbonyl complexes. Despite attempts at their liberation from the Mo(0) template complexes, the macrocyclic ligands were unknown in the free, uncoordinated state prior to our present study and there are no other stereospecific syntheses of uncoordinated triphosphorus macrocycles. We have recently reported the derivatization of the trisecondary phosphine macrocycle complexes to corresponding tritertiary phosphine complexes,[5] selective oxidations by halogens to seven coordinate Mo(II) complexes,[6] and the extension of this template route to Cr.[7] In this paper, we report the stereospecific syntheses of 1,5,9-triphosphacyclododecane and a number of tritertiary derivatives by liberation from their Mo(II) and Cr(II) templates. Preliminary results of this study have recently appeared.[8]

Experimental Section

All reactions were carried out in an atmosphere of dry nitrogen. All solvents were dried by boiling under reflux over standard drying agents. Petroleum ether had bp 40−60 °C. The compounds $[(R_3L)Mo(CO)_3]$ (R = $(CH_3)_2CH$, $(CH_3)_3SiCH_2$;[5] R = Et, ^iBu[9]), $[(R_3L)Mo(CO)_2X_2]$[6] (X = Cl, Br, I; R = Et, ^{i}Bu, $(CH_3)_2CH$, $(CH_3)_3SiCH_2$), and $[(H_3L)Cr(CO)_3]$[7] were prepared as previously described. All other chemicals were obtained from the Aldrich Chemical Co. and used without further purification except alkyl halide reagents which were dried over molecular sieves and deoxygenated by freeze-thaw degassing. NMR spectra (Table 1) were recorded on a Bruker WM360 instrument at 360.13 (^1H), 90.53 MHz (^{13}C) or a Jeol FX-90Q instrument operating at 36.23 MHz (^{31}P). All NMR spectra were recorded in $CDCl_3$ solution unless otherwise stated, ^1H and ^{13}C NMR

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chemical shifts are quoted in ppm relative to solvent resonances (δ 7.27, ^{1}H; δ 77.0, ^{13}C), and ^{31}P NMR chemical shifts are quoted in ppm relative to external 85% H_3PO_4 ($\delta = 0$ ppm). All chemical shifts are positive to low field of the standards. Infrared spectra were recorded in Nujol on a Nicolet 510 FT-IR spectrometer. Magnetic susceptibilities were measured by the Gouy method on a Johnson Matthey magnetic susceptibility balance; an experimental diamagnetic correction was measured for *cyclo*-$(HPC_3H_6)_3$ and applied. Mass spectra (EI, Table 1) were recorded on a VG Platform II Fisons mass spectrometer. Melting points were obtained in sealed capilliaries and are uncorrected.

Preparations: 1,5,9-Trialkyltriphosphacyclododecane [(R_3L) (R = 2-Propyl (6), (Trimethylsilyl)methyl (7), Ethyl (8), Isobutyl (9)]. A suspension of $[(R_3L)MoX_2(CO)_3]$ (0.30 mmol, X = Br, I) in ethanol (30 cm^3) was stirred at room temperature for 16 h. The mixture was cooled to 0 °C and a large excess of NaOH pellets (> 1.0 g) added. The mixture was allowed to warm to room temperature and stirred for a further 4 h. The solvent was removed *in vacuo* to give an oily gray residue. The mixture was cooled to 0 °C, H_2O (30 cm^3) was added and the mixture was allowed to warm to room temperature and stirred for 1 h. The product appeared as an oily upper layer and was extracted with petroleum ether (3 × 50 cm^3). The combined organic phases were dried over $MgSO_4$ overnight. The $MgSO_4$ was removed by filtration and the solvent removed *in vacuo* to give the product as a white solid. Mp: 114.8−115.3 °C for **6**; 112.0−114.1 °C for **7**; 103−106 °C for **8**; 120.0−121.5 °C for **9**. IR (neat thin film): (**6**) 2968 s, 2922 s, 2864 m, 1468 m,1420 m, 1257 (sh), 1096 s, 1026 s, 700 (br), 664 m; (**7**) 2964 s, 2922 s, 1257 (sh), 1110 s, 1026 s, 702 br; (**8a**) 2966 s, 2917 s, 2860 (br), 1458 (br), 1422 m, 1377 m, 1257 (sh), 1096 s, 1026 s, 864 m, 801 s, 723 m, 702 br, 660 w, 480 w; (**9**) 2978 s, 2918, 2840 m, 1461 m, 1367 m, 1257 (sh), 1096 s, 1026, 913 m, 801 m, 703 (br), 667 m.

1,5,9-Triphosphacyclododecane, H_3L (13). To a solution of $(H_3L)Cr(CO)_3$ (**10**) (1.0 g, 2.8 mmol) in CH_2Cl_2 (50 cm^3) was added a solution of Cl_2 or Br_2 (8.7 mmol) in CH_2Cl_2 (20 cm^3) dropwise at room temperature, immediately forming a violet-blue precipitate. The mixture was filtered and the residue washed with CH_2Cl_2 (2 × 20 cm^3) and then dried *in vacuo* to give $(H_3L)Cr(CO)_3X_2$, **11** (X = Cl) and **12** (X = Br), in 60% and 65% yield respectively, which were used for the next step without further purification. Ethanol (50 cm^3) was added to form a blue suspension which was stirred at room temperature for 16 h. The mixture was cooled to 0 °C and a large excess of NaOH pellets (>1.0 g) added. The mixture was allowed to warm to room temperature and stirred for a further 4 h. The solvent was removed *in vacuo* to give a gray residue which was taken into cooled H_2O (30 cm^3, 0 °C), allowed to warm to room temperature, and stirred for 1 h. The product was extracted with petroleum ether (40−60 °C) (3 × 50 cm^3). The combined organic phases were dried over $MgSO_4$ overnight. The $MgSO_4$ was removed by filtration and the solvent removed *in vacuo* to give the product as a white oil, mp *ca*. 10 °C (yield: 0.25 g, 40% based on **10**). Anal. (C.H.N. Analysis Ltd, Leicester, U.K.) found (calcd): for **11** ($C_{11}H_{21}Cl_2O_2P_3Cr$), C, 32.39 (32.92); H, 5.24 (5.97); for **12** ($C_{11}H_{21}Br_2O_2P_3Cr$), C, 25.91 (26.93); H, 4.29 (4.79); for **13** ($C_9H_{21}P_3$), C, 47.81 (48.65); H, 9.28 (9.46). IR (neat thin film): 2974 s, 2922 s, 2866 s, 2277 (sh), 1458 m, 1428 m, 1368 m, 1260 (sh), 1096 s, 1026 s, 864 m, 801 s, 698 br, 664 m.

Macrocycle Phosphine Oxides [(R_3O_3L)] (R = 2-Propyl (14), (Trimethylsilyl)methyl (15), Ethyl (16a), (16b), Isobutyl (17), H (18), Methyl (27), *tert*-Butyl (28)). A solution of (R_3L) in toluene (20 cm^3) was left exposed to air for 2 weeks. The products were identified by ^{31}P NMR which indicated purities >95% in all cases. δ (^{31}P) ppm ($CDCl_3$): **14**, +54.3; **15**, +46.0; **16a**, +40.3; **16b**, +42.9(t), +38.3-(d), $^4J_{PP}$ = 60 Hz; **17**, +49.0; **18**, +30.2 (d, $^1J_{PH}$ = 445 Hz); **27**, +40.6 (t), +36.6 (d), $^4J_{PP}$ = 66 Hz; **28**, +65.0 (t), +58.6 (d), $^4J_{PP}$ = 65Hz.

Alternative Preparations of [(R_3O_3L)](14). Method 1. A solution of $[(^iPr_3L)Mo(CO)_3]$ (0.10 mmol) in CH_2Cl_2 (30 cm^3) was cooled to 0 °C and a stream of ozone in air (approximately 5%) was bubbled through the solution for 10 min. Nitrogen was bubbled through the solution to purge the solution of ozone, and then solvent was removed *in vacuo* to give an off-white solid. A suspension of this product in ethanol (30 cm^3) was stirred at room temperature for 16 h. The mixture was cooled to 0 °C and a large excess of NaOH pellets (>1.0 g) added. The mixture was allowed to warm to room temperature and stirred for a further 4 h. The solvent was removed *in vacuo* to give an oily gray residue which was cooled to 0 °C, H_2O (30 cm^3) was added and the mixture allowed to warm to room temperature and stirred for 1 h. The product was extracted with petroleum ether (3 × 50 cm^3). The combined organic phases were dried over $MgSO_4$ overnight. The $MgSO_4$ was removed by filtration and the solvent removed *in vacuo* to give $^iPr_3O_3L$ (**14**) as a white solid (yield: 87%).

Method 2. A solution of $[(^iPr_3L)Mo(CO)_3]$ (0.10 mmol) in toluene (30 cm^3) was refluxed with H_2O_2 solution (30% w/v) for 48 h. During this time a blue solid was formed. The solvent was removed *in vacuo* (*Caution*! incomplete decomposition of H_2O_2 could result in explosion) to give a blue solid. A suspension of this product was stirred in ethanol (30 cm^3) at room temperature for 16h. The mixture was cooled to 0 °C and a large excess of NaOH pellets (>1.0 g) added. The mixture was allowed to warm to room temperature and stirred for a further 4 h. The solvent was removed *in vacuo* to give an oily gray residue which was cooled to 0 °C, H_2O (30 cm^3) was added, and the mixture was allowed to warm to room temperature and stirred for 1 h. The product was extracted with petroleum ether (3 × 50 cm^3) and the combined organic phases dried over $MgSO_4$ overnight. The $MgSO_4$ was removed by filtration and the solvent removed *in vacuo* to give $^iPr_3O_3L$ (**14**) as a white solid (yield: 91%).

Trihydrochloride Compounds $(R_3H_3L)^{3+}$ (R = 2-Propyl (19), (Trimethylsilyl)methyl (20), Ethyl (21), Isobutyl (22)). A dried stream of HCl gas in nitrogen was bubbled through a cooled (−20 °C) solution of (R_3L) in diethyl ether (30 cm^3), immediately causing the separation of a white precipitate. When formation of the precipitate ceased, the addition of HCl was stopped and nitrogen was bubbled through the solution to purge the solution of excess HCl. The white product was filtered and washed with diethyl ether (3 × 10 cm^3) (yield: 80−92%). The products were identified by ^{31}P NMR. δ (^{31}P) ppm (CD_3OD): **19**, +21.1; **21**, +13.1; **22**, +4.0. δ (^{31}P) ppm ($CDCl_3$): **20**, +6.0.

$(H_6L)^{3+}$ (23). To degassed aqueous hydrochloric acid (10 cm^3, 10 M) was added H_3L (0.30 mmol) at ambient temperature and the mixture stirred (2 h), at which time the aqueous insoluble trisecondary phosphine had dissolved. The colorless solution was evaporated to dryness *in vacuo*, leaving a white solid which was washed with diethyl ether and identified by ^{31}P NMR (yield: quantitative). δ (^{31}P) ppm ($CDCl_3$): −23.7 (t), $^1J_{PH}$ = 522 Hz.

***syn,anti*-(R_3L) (R = CH_3 (24), *t*-Bu (25)).** To a cooled (−78 °C) solution of H_3L (0.30 mmol) in tetrahydrofuran (thf) (20 cm^3) was added a solution of *n*-BuLi (0.9 mmol) in hexane (1 cm^3) dropwise and the mixture allowed to slowly warm to −20 °C. The mixture was then recooled to −78 °C and RX (0.90 mmol, RX = CH_3I (for **24**), *t*-BuCl (for **25**)) was added dropwise. The mixture was allowed to slowly warm to room temperature and then stirred for 30 min. The solvent was removed in *vacuo* to give a pale colored oil that was dissolved in CH_2Cl_2 (30 cm^3) and passed through a short silica column (5 cm) with CH_2Cl_2 as eluant. Evaporation *in vacuo* gave the desired product which was then recrystallized from petroleum ether at −20 °C (yield: 80−90%). IR (neat thin film): (**24**) 2966 s, 2924 s, 2854 m, 1447 m, 1412 m, 1264 (sh), 1096 s, 1026 s, 700 s, 684 m, 654 m; (**25**) 2968 s, 2928 s, 2862 m, 1478 m, 1422 m, 1412 m, 1257 (sh), 1096 s, 1026 m, 864 m, 801 s, 700 s, 684 m, 658 m.

***syn,anti*-(Et_3L_b) (8b).** A solution of H_3L (0.30 mmol) and AIBN [2,2′-azobis(2-methylproprionitrile)] (*ca*. 1%) in toluene (20 cm^3) was frozen at −196 °C in a glass pressure reaction flask. A large excess (>1.0 g) of C_2H_4 was added and the mixture heated to 80 °C for 3 h. The mixture was allowed to cool to room temperature and then filtered through a short (4 cm) Celite column to give a colorless solution. The solvent was removed *in vacuo* and the product obtained as a colorless oil from petroleum ether solution at −20 °C (yield: 80%). IR (neat thin film): 2968 s, 2922 s, 2860 m, 1458 m, 1422 m, 1356 m, 1260 (sh) 1096 s, 1026 s, 864 (br), 799 s, 700 (br).

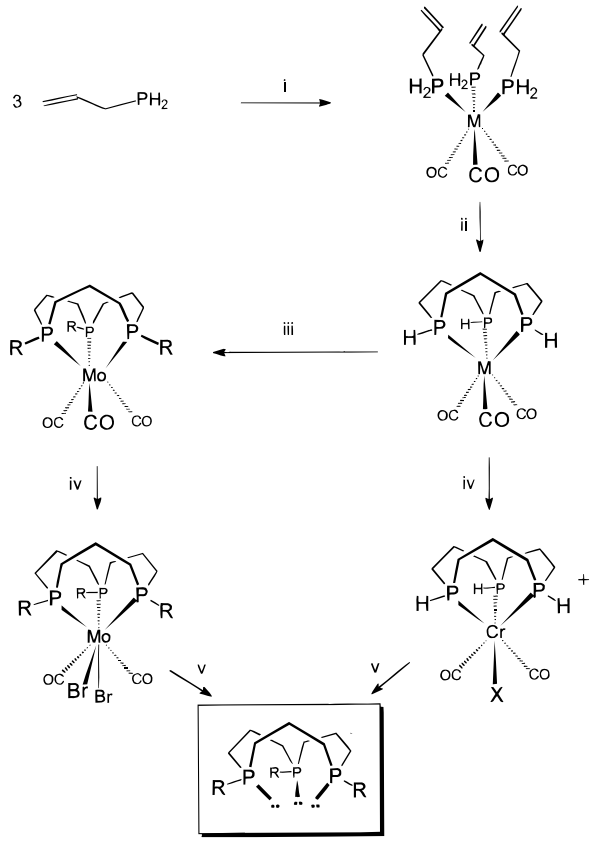
Results and Discussion

Molybdenum Macrocycle Complexes. The Mo(0) complexes $(R_3L)Mo(CO)_3$ (R_3L = 1,5,9-trialkyl-1,5,9-triphosphacyclododecane) are remarkably resistant to dissociation of the macrocyclic ligand and are inert with respect to ligand displace-

ment under a range of conditions including digestion in HCl(*l*), SO_2(*l*), and DMSO/KCN (DMSO = dimethyl sulfoxide) and carbonyl substitution in CH_3CN/Me_3NO. These octahedral d^6 Mo(0) complexes are expected to be inert to both associative or dissociative substitutions. In order to overcome inertness arising from ligand field stabilization, selective oxidations of the metal would be more likely to enable successful displacement of the macrocycle. Oxidation of these Mo(0) complexes by halogen is facile and selective and initially forms the Mo(II) salts $[(R_3L)Mo(CO)_3X]^+X^-$ (X = Cl, Br, I).[6] However, if liberation of the macrocycle from these halo−halide complexes is attempted by digestion in strongly basic alcoholic solution, the only product observed in the $^{31}P\{^1H\}$ NMR spectrum corresponds to the Mo(0) complex, $(R_3L)Mo(CO)_3$. This apparent relative instability of the halo−halide complexes is illustrated by the behavior of $[(^iPr_3L)Mo(CO)_3I]BPh_4$ (**1**) at elevated temperatures. This complex was chosen for study because the possibility of competing carbonyl substitution by external halide to form a complex of the type $[(R_3L)Mo(CO)_2X_2]$ is excluded. Compound **1** was heated to 55 °C [above the coalescence temperature of the complex in the $^{31}P\{^1H\}$ NMR spectrum (The seven coordinate halogeno−halide Mo(II) complexes exhibit fluxional behavior in their ^{31}P NMR spectra where A_2B patterns are observed at the low temperature limit; for **1**, $T_c = 27$ °C.[6])]) during which process, a peak at δ 11.2 ppm in the $^{31}P\{^1H\}$ NMR spectrum corresponding to $[(^iPr_3L)Mo(CO)_3]$[5] grows ($t_{1/2}^{55\,°C} = 50 \pm 5$ min) and $(^iPr_3L)Mo(CO)_3$ may be reclaimed in good yield (>80%) after 8 h. This observation explains why attempts to increase the rate of the surprisingly slow conversion the of halo−halide complex to the corresponding dihalo−dicarbonyl complex by heating cause a significant decrease in yield of the desired dihalo product. The nature of the oxidation products formed during the reduction of the Mo(II) salts was not determined; however, as the reduction occurs in higher yield than anticipated for a disproportionation, it is reasonable to presume that solvent that acts as the reductant.

Liberation of Tritertiary Phosphine Macrocycles. The reaction of the neutral Mo(II) tritertiary macrocycle dicarbonyl complexes $[(R_3L)Mo(CO)_2X_2]$ [X = Cl, Br, I; R = $(CH_3)_2CH$, ^{i}Pr (**2**); $(CH_3)_3SiCH_2$ (**3**); C_2H_5, Et (**4**), $(CH_3)_2CHCH_2$, ^{i}Bu (**5**)] with NaOH in alcoholic solution results in the loss of color due to the Mo(II) complexes; evaporation of the mixture followed by extraction of the residue with water results in the separation of an oily phase from which the free macrocycles, R_3L [R = $(CH_3)_2CH$ (**6**), $(CH_3)_3SiCH_2$ (**7**), C_2H_5 (**8**), $(CH_3)_2CHCH_2$ (**9**)], may be isolated in high yield (75−80%). Since the same reaction conditions cause the intermediate Mo(II) halo−halide complexes $[(R_3L)Mo(CO)_3X]^+X^-$ to be reduced to the Mo(0) precursor complex, the presence of this intermediate in the dihalo−dicarbonyl complexes $[(R_3L)Mo(CO)_2X_2]$ significantly depletes the yield of the macrocycle upon liberation. All macrocycles are white, crystalline solids and were characterized by $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopy, mass spectrometry, and IR spectroscopy; NMR and mass spectroscopic data are collected in Table 1. Compound **6** has also been characterised structurally[8] and the parent of the series, **13**, analytically. In all cases, the $^{31}P\{^1H\}$ NMR spectra exhibit singlets, which indicate that the liberation is stereospecific (*i.e.* all phosphorus lone pairs lie on the same side of the molecule in a *syn*, *syn* conformation as in isomer **a**, Figure 1). In their ^1H NMR spectra, resonances attributable to the α (PCH_2) ring protons for all the free macrocycles fall in the region δ 1.85−1.70 ppm and those assigned to the β (PCH_2CH_2) ring protons fall in the region δ 1.65−1.30 ppm. In the $^{13}C\{^1H\}$ NMR spectra, carbons assigned to PCH_2 are observed between δ 24.0 and 30.2 ppm and those due to PCH_2CH_2 are in the range δ 18.8−22.8 ppm. These values show only small differences from those observed in the parent Mo(0) complexes.

Scheme 1[a]



[a] Key: (i) $(CH_3CN)_3M(CO)_3$, PhMe, M = Cr, Mo; (ii) AIBN, PhMe, 80 °C; (iii) 3BuLi, 3RX, R = ^{i}Pr, Me_3SiCH_2, X = halide, THF; (iv) X_2, CH_2Cl_2, X = Cl, Br; (v) NaOH, EtOH.

An alternative method for the liberation of the free macrocycle, by addition of $[(^iPr_3L)MoBr_2(CO)_2]$ to a refluxing solution of KCN in dimethyl sulfoxide, also results in the formation of $^iPr_3L$ (**6**) in good yield. Again, if the same reaction is performed with the halo−halide complex $[(^iPr_3L)MoBr(CO)_3]Br$, the Mo(0) complex $[(^iPr_3L)Mo(CO)_3]$ is the only product observed in the $^{31}P\{^1H\}$ NMR spectrum. Clearly, the liberation by digestion in base is more convenient; the identity of the Mo-containing species generated as a by-product in either liberation reaction was not investigated. It has previously been reported that addition of an excess of halogen in oxidations of Mo(0)−phosphine complexes results in the formation of phosphine oxide complexes.[10] This is confirmed for the addition of an excess of Cl_2 to the tertiary macrocycle complexes **2** and **3**. Digestion of the subsequent products from these reactions in alcoholic base does indeed liberate a mixture of the free macrocycle and partially oxidized derivatives. These phosphine oxide macrocycles (*vide infra*) can be separated from the phosphines by washing with deoxygenated water.

Chromium Macrocycle Complexes. Neither of the methods described, however, cause the liberation of the trisecondary compound 1,5,9-triphosphacyclododecane from $(H_3L)MoX_2(CO)_2$ (X = Cl, Br, I). Although this is surprising, this may be due to the very poor solubility of these complexes in all common solvents. A route to the trisecondary macrocycle was successfully developed by oxidation of the chromium complex $[(H_3L)Cr(CO)_3]$ (**10**) followed by liberation by base. Complex **10**

(10) Moss, J. R.; Shaw, B. L. *J. Chem. Soc. A* **1970**, 595

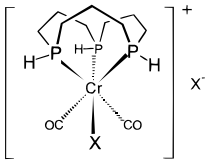
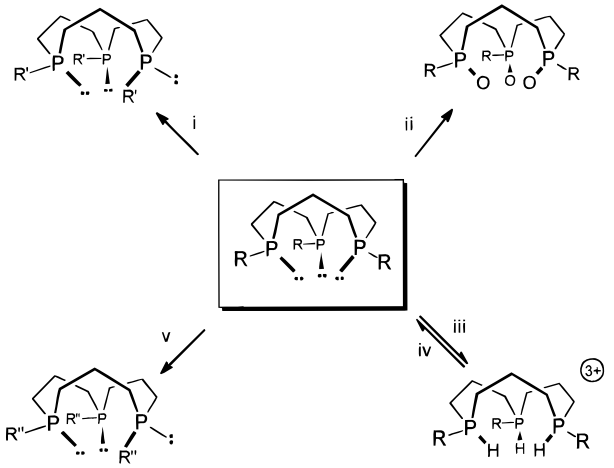


Figure 2. Proposed structure for **11** and **12** (X = Cl, Br).

undergoes rapid reactions with Br_2 or Cl_2 to give intensely violet-blue colored and poorly crystalline solids for which elemental analyses support the empirical formula $[(H_3L)Cr(CO)_2X_2]$ (for **11**, X = Cl; for **12**, X = Br). Both complexes are paramagnetic ($\mu_{eff} = 2.61$ μB for **11**, $\mu_{eff} = 2.72$ μB for **12**) and ESR silent and exhibit only two stretches in the ν(CO) region of the IR spectrum (at 1918 and 1813 cm^{-1} and 1918 and 1827cm^{-1}, respectively); owing to the poor solubility of both complexes in common organic solvents, further solution spectroscopic data were not obtained. Although **11** and **12** are empirically analogous to the Mo(II) and W(II) complexes formed under the same conditions, examples of seven coordinate Cr(II) complexes are uncommon, the most closely related complexes $\{[Cr(CO)_2diars_2X]^+$; diars = 1,2-bis(dimethylarsino)-benzene, X = halide[11] $\}$ are diamagnetic as are the isonitriles $[Cr(CNR)_7]^{2+}$, $[Cr(CNR)_5(dppe)]^{2+}$, $[Cr(CNR)_5(dppe)]^{2+}$ [R = aryl,[12a] alkyl,[13] dppe = 1,2-bis(diphenylphosphino)ethane; dppm = 1,2-bis(diphenylphosphino)methane] and the dihydride $Cr[P(OMe)_3]_5H_2$;[14] however, the paramagnetic six coordinate Cr(II) isonitrile[12] and dihalo tertiary phosphine complexes $[X_2Cr(dmpe)_2$; X = Cl, Me; dmpe = 1,2-bis(dimethylphosphino)-ethane][15] are low spin with magnetic susceptibilities similar to those of **11** and **12** $\{\mu_{eff} = 2.59$ μ_B for $[CrCl(CNPh)_3(dppe)](PF_6)$ to 3.14 μ_B for $[Cr(CNPh)_6](PF_6)_2\}$; the dmpe complexes are ESR silent as are **11** and **12** (in the solid state over the range 300−77 K) which would not be expected if they were compounds of Cr(I) or Cr(III). In contrast, the series of cationic Cr(II) halides with the quadridentate tripodal ammine, ammine/phosphine, and phosphine ligands $N(CH_2CH_2NMe_2)_3$, $N(CH_2CH_2PPh_2)(CH_2CH_2NEt_2)_2$,[16] $N(CH_2CH_2PPh_2)_3$, $N[CH_2CH_2P(C_6H_{11})_2]$,[17] and $P(CH_2CH_2PPh_2)3$[18] are high spin. Thus our data are consistent with **11** and **12** being six coordinate low spin d^4, Cr(II) salts (of the type in Figure 2) and the behavior of the Cr(0) macrocycle complex with halogens appears to differ from that of Mo in that the initial oxidation also results in loss of one carbonyl ligand and renders the Cr(II) product susceptible to liberation directly, without the need for the slow conversion of halo−halide into dihalo complexes.

Synthesis of 1,5,9-Triphosphacyclododecane. Digestion of **11** or **12** in strongly basic alcoholic solution gives rise to the free, uncoordinated trisecondary macrocycle (H_3L, **13**) as a low-melting (∼ 10 °C), white solid in approximately 40% yield.

Scheme 2[a]



[a] Key: R = H, Et, ^{i}Pr, ^{i}Bu, Me_3SiCH_2; R′ = Et or ^{i}Bu; R″ = Me, ^{t}Bu. (i) C_2H_4 or CH_2CMe_2, AIBN, PhMe, 80 °C; (ii) air; (iii) $HCl_{(aq)}$; (iv) $NaOH_{(aq)}$; (v) 3BuLi, 3R″X, X = halide, THF.

This low yield may be related to the formation of HCl and HBr during the oxidation reaction, which were identified (indicator, $AgNO_3$) and determined by titration of a solution of the trapped exhaust gases. The amount of HX formed increases as the reaction temperature is lowered with consequent lowering of the yield of free macrocycle during the liberation process. Best yields of **13** were obtained when the reaction was performed at room temperature, although even under these conditions approximately 25% of halogen added (in a stoichiometric reaction) results in the formation of HX. Oxidation with a less than stoichiometric amount of halogen still forms HX with unreacted Cr(0) precursor complex **10** remaining in solution; unlike the behavior of the Mo tertiary phosphine complexes, addition of excess halogen to **10** does not result in oxidation of the macrocycle.

Reactions of Triphosphorus Macrocycles. The phosphine macrocycles are air-sensitive and partially oxidise rapidly in solution when left open to air but complete oxidation to form the 1,5,9-trioxides [R_3O_3L; R = $(CH_3)_2CH$ (**14**), $(CH_3)_3SiCH_2$ (**15**), C_2H_5 (**16**), $(CH_3)_2CHCH_2$ (**17**), H (**18**)] takes several days, even if air is bubbled through the solution. In all cases, singlets were observed in the $^{31}P\{^1H\}$ NMR spectra of the tertiary phosphine oxides and at approximately 70−90 ppm downfield from the free tertiary phosphines (for the secondary phosphine oxide $\Delta\delta = 115$ ppm). The formation of H_3O_3L by exposure of *cyclo*-$(HPC_3H_6)_3$ to air was monitored by IR spectroscopy, a new peak due to ν(P═O) appears at 1138 cm^{-1} over several hours. IR spectroscopy also shows that the phosphine oxides are hygroscopic with new peaks at 3430 (br s) and 1651 cm^{-1} (br) corresponding to the presence of hydroxy functions. The partially oxidized intermediates can be studied by $^{31}P\{^1H\}$ NMR spectroscopy; if a sample of (H_3L) in CH_2Cl_2 is left open to air for 2 days, peaks are observed that can be attributed to unoxidized H_3L (δ −81.6), H_3O_3L (δ +27.4) and also a triplet (δ −84.3, $J_{PP} = 60$ Hz) and a doublet (δ +29.4, $J_{PP} = 60$ Hz), corresponding to a partially oxidized species containing two phosphine oxide groups and one phosphine group (resonances attributable to a monoxide were not observed).

In our attempts to liberate the free macrocycle, the reactions of $[(^iPr_3L)Mo(CO)_3]$ with H_2O_2 and O_3 were investigated. These reactions gave rise to blue and colorless products respectively. IR spectroscopy showed the absence of bands in the ν(CO) region for either complex but we were unable to fully characterize these compounds. However, digestion of the

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(18) Mani, F.; Saccioni, L.; Stoppioni, P. *J. Chem. Soc., Dalton Trans*. **1975**, 461.

oxidation products in strongly basic alcoholic media liberated the free triphosphaoxide macrocycle, *cyclo*-({CH_3}$_2$CHP(O)-C_3H_6)$_3$, in good yield (>85%), clearly suggesting that both these oxidants oxidize the phosphorous atoms as well as the metal center.

Addition of dry HCl gas to a solution of the free macrocycles (R_3L) in apolar solvents results in the precipitation of the trihydrochloride salts [$(H_3R_3L)^{3+}$; R = $(CH_3)_2CH$ (**19**), $(CH_3)_3SiCH_2$ (**20**), C_2H_5 (**21**), $(CH_3)_2CHCH_2$ (**22**)], which were identified by $^{31}P\{^1H\}$ NMR only. Under similar reaction conditions however, the trisecondary phosphine **13**, gives rise to a mixture of mono; di-, and trihydrochlorides which were identified by singlets in the $^{31}P\{^1H\}$ NMR spectra of their aqueous (D_2O) solutions (δ −23.7, −49.1, −69.4 ppm, respectively) indicating lability of H^+ in the mono- and dihydrochlorides. Similar behavior is observed upon addition of HBF_4 solution to **13**; again the $^{31}P\{^1H\}$ NMR spectrum of an aqueous solution indicates the formation of all three hydrochlorides (δ −34.8, −44.64, −53.2 ppm), but addition of aqueous HCl solution to **13** gives solely the expected trihydrochloride compound $(H_6L)^{3+}$ (**23**). Subsequent addition of aqueous NaOH solution results in the deprotonation of these salts and the quantitative formation of the free triphosphamacrocycles in all cases.

Since secondary phosphines are readily functionalized to tertiary derivatives by either deprotonation of the P−H function with base followed by alkylation with alkyl halide or by radical catalyzed addition of the P−H function to an alkene group, we have investigated these reactions with the free trisecondary macrocycle **13**. Deprotonation of **13** with *n*-BuLi followed by addition of alkyl halide RX (RX = MeI, *tert*-BuCl) gives rise to a single product in almost quantitative yield, *syn,anti*-(Me_3L) (**24**) and *syn,anti*-($^tBu_3L$) (**25**), respectively. The reaction of **13** with excess ethene in the presence of AIBN results in the formation of *syn,anti*-(Et_3L_b) (**8b**), again in good yield (80%). Molecular ions are observed in the mass spectra for all three compounds. The $^{31}P\{^1H\}$ NMR spectra however are not singlets. A_2B patterns are observed for **24** (δ −38.3 (t), −49.5 (d)), **25** (δ −9.9 (t) and −15.7 (d) ppm) and for **8b** (δ −29.4 (t), −38.7 (d)). The ^1H and $^{13}C\{^1H\}$ NMR spectra are correspondingly more complex than those for the other isomeric tritertiary phosphine macrocycles described here. This NMR data clearly indicates that alkylation of the free trisecondary macrocycle **13** by either of these two routes is not stereospecific, as would be expected, resulting in the predominant formation of the alternative *syn,anti* isomer **b** (Figure 3) where one phosphorus atom is inverted with respect to the other two and the plane of the ligand. This isomer is also reported to be thermodynamically more stable for the triphosphorus macrocycles reported by Kyba[2] and is not likely to be so readily disposed to coordinating mononuclear complexes (at least as a tridentate ligand).

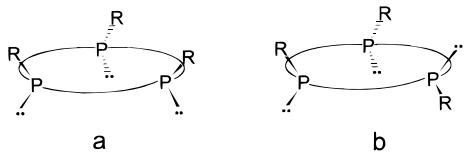

Figure 3. Possible conformational isomers of 1,5,9-triphosaphacyclododecane and tertiary derivatives (R = H, alkyl).

The behavior of the free ligand in these reactions demonstrates the value of the alkylation route on the metal-template prior to liberation, resulting in the more useful isomer, **a**. In order to obtain a qualitative estimation of the relative stability of isomer **a**, the conversion of **8a** into **8b** was followed by $^{31}P\{^1H\}$ NMR of **8a** in refluxing mesitylene (bp 156 °C). At this temperature, peaks at δ −29.4 and −38.7 ppm, indicating the presence of isomer **8b**, could be observed after 20 min, and the half-life of the conversion was estimated to be approximately 20 h.

Conclusion

The first stereoselective synthesis of trisecondary and tritertiary phosphorus macrocycles has been developed by prior oxidation of the kinetically inert chromium and molybdenum template complexes; these new ligands are available in good yield by this route and a range of phosphorus substituents are readily incorporated by well-established alkylation methods. The free macrocycles also constitute the first symmetrical triphosphorus macrocycles available as ligands for general application in coordination chemistry thus limiting potential complications arising from complex isomeric mixtures. They have features of interest, being neutral, 6-electron tridentate ligands that will preferentially coordinate mutually *cis* sites in their metal complexes; the study of their coordination complexes will no doubt also be of interest.

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