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TRANSITION METAL—CARBON BONDS

XLIV *. ORGANO-TRANSITION METAL COMPLEXES CONTAINING CROWN ETHER GROUPS

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Summary

Some benzo-crown ethers, substituted in the arene ring, are described e.g. 15-X-substituted benzo-15-crown-5 ether (1, X = C≡CPh, CH=CHCOOH, CH=CHCOOMe, CH=CHCOOEt, CH=CHCOCl). 15-Iodo-benzo-15-crown-5 and 18-iodo-benzo-18-crown-6, oxidatively add to $Pd(PPh_3)_4$ to give *trans*-$[PdIR(PPh_3)_2]$, (R = (2) or (3)). $[Pt(stilbene)(PPh_3)_2]$ reacts similarly with the aryl iodides to give *trans*-$[PtIR(PPh_3)_2]$ (R = (2), (3), (4) or 3,4-dimethoxyphenyl. The platinum complexes with R = (2), (3) or (4) appear to form adducts with sodium iodide in solution. *trans*-$[PtIR(PPh_3)_2]$ was converted to the corresponding thiocyanate and chloride (via the nitrate). PhC≡CR (R = (2) or 3,4-dimethoxyphenyl) react with *cis*-$[PtCl_2(PPh_3)_2$ in the presence of hydrazine to give $[Pt(PhC{\equiv}CR)(PPh_3)_2]$ and PhC≡CR react with $[Co_2(CO)_8]$ to give $[Co_2(PhC{\equiv}CR)(CO)_6]$, with $Ni(C_5H_5)_2$ to give $[Ni_2(C_5H_5)_2(PhC{\equiv}CR)]$ and with $W(CO)_6$ in acetonitrile to give $[W(CO)(PhC{\equiv}CR)_3]$; PMe_2Ph displaces the CO from $[W(CO)(PhC{\equiv}CR)_3]$ to give $[W(PMe_2Ph)(PhC{\equiv}CR)_3]$. $[Cr(CO)_6]$ reacts with the benzo-crown ethers RH, R = (2), (3) or (4) or with 1,2-dimethoxybenzene to give yellow arenechromium tricarbonyl complexes of the type $[Cr(CO)_3(RH)]$. $[Cr(CO)_3(benzo\text{-}15\text{-}crown\text{-}5)]$ forms a green 1/1 adduct with NaSCN.

Introduction

There is currently great interest in the chemistry of crown ethers: see for example refs. 2—5. Crown ethers form complexes with alkali metal, alkaline-earth metal and some other metal ions, with oxonium ions, protonated amines

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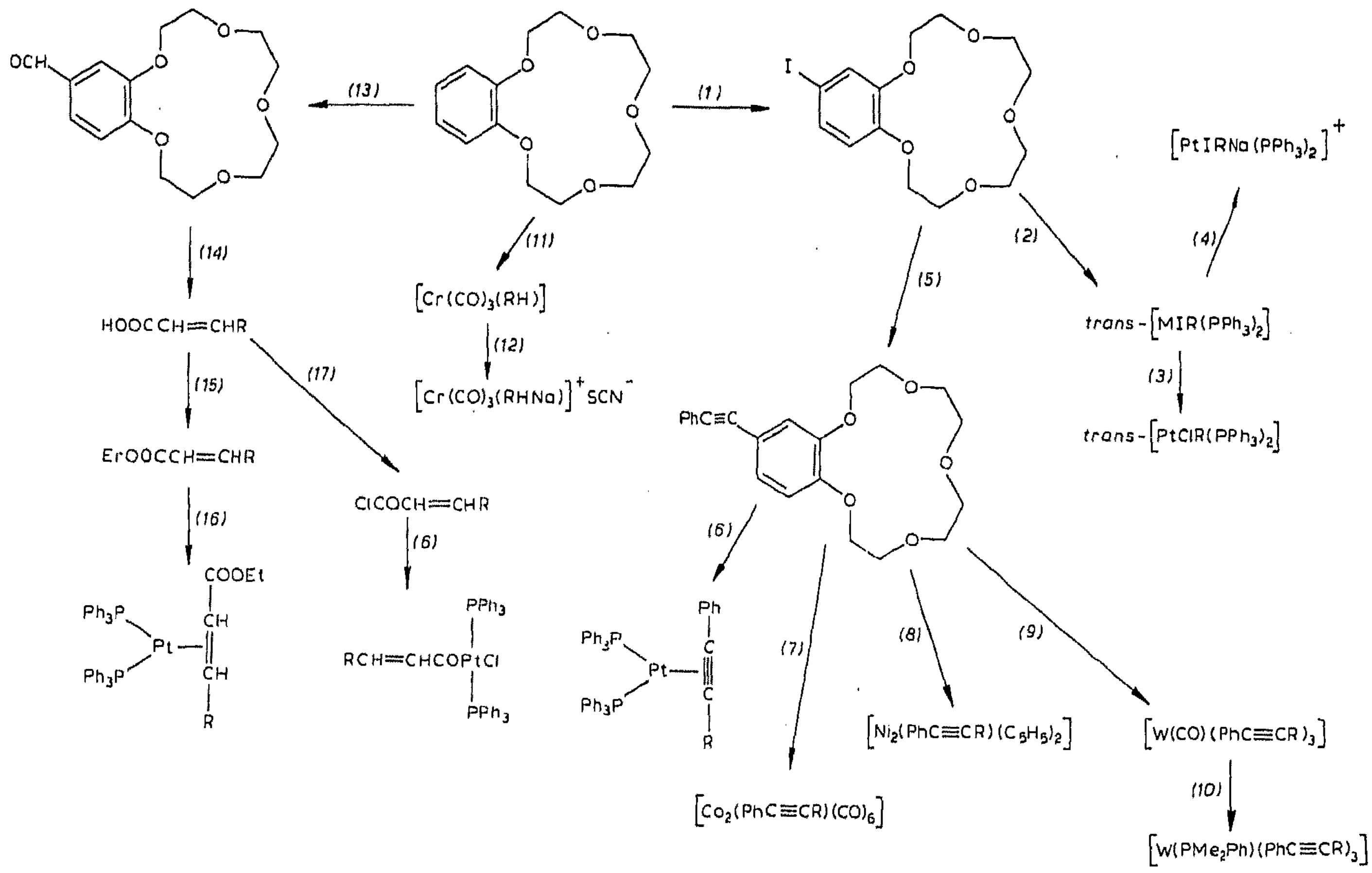
* For Part XLIII see ref. 1.

SCHEME 1. Some derivatives of benzo-15-crown-5 and their complexes with transition metals. R = the 15-substituted benzo-15-crown-5 radical (2). (*1*) = HIO_4/I_2, (*2*) = $[Pd(PPh_3)_4]$ or $[Pt(stilbene)PPh_3)_2]$, (*3i*) = $AgNO_3$, (*3ii*) = LiCl, (*4*) = NaI, (*5*) = $CuC{\equiv}CPh$/pyridine, (*6*) = $[Pt(stilbene)(PPh_3)_2]$, (*7*) = $[Co_2(CO)_8]$, (*8*) = $[Ni(C_5H_5)_2]$, (*9*) = $[W(CO)_6]/CH_3CN$, (*10*) = PMe_2Ph, (*11*) = $[Cr(CO)_6]$, (*12*) = NaSCN, (*13*) = $POCl_3/CHONMePh$, (*14*) = $CH_2(COOH)_2$/piperidine/pyridine, (*15*) = $EtOH/H^+$, (*16*) = $[Pt(C_2H_4)(PPh_3)_2]$, (*17*) = $SOCl_2$.



including amino acids and also with some rod-like molecules or ions. They are particularly useful in phase-transfer catalysis. Simple crown ethers are, however, very poor ligands for transition metal ions (except Ag^+) [6].

We are carrying out a programme of research to introduce donor atoms or groups into crown ethers so that they would become good ligands for transition metals: the resultant complexes would thus combine properties of a transition metal compound and a crown ether within the same molecule. We have described some transition metal complexes containing tertiary phosphine substituted crown ethers as ligands [7]. In the present paper we report on a variety of organometallic compounds in which the organic grouping attached to the transition metal contains a crown ether moiety and is joined to the metal by metal—carbon σ- or π-bonds. Metal-aryl, -acyl, -olefin and -acetylene (bridging and non-bridging) and metal—arene complexes are described. The chemistry of compounds containing the benzo-15-crown-5 residue is summarized in Scheme 1. We also describe analogous compounds containing the 3,4-dimethoxyphenyl group i.e. model compounds for comparison with the complexes containing crown ether moieties.

Results and discussion

We have reported in a previous paper the preparation of 15-iodo-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin * abbreviated to 15-iodobenzo-15-crown-5. (1, X = I) and the corresponding 18-iodobenzo-18-crown-6 [7]. We now find that these aryl iodides readily react with the palladium(0) complex $[Pd(PPh_3)_4]$ to give the arylpalladium(II) complexes *trans*-$[PdIR(PPh_3)_2]$, R = (2) or (3) respectively. Microanalytical data are given in Table 1. Both their ^1H NMR spectra ($CDCl_3$), show unresolved multiplets δ 5.7—8.0 ppm (aryl protons) and δ 3.0—4.0 ppm (crown ether methylene protons). Both show a singlet ^{31}P NMR resonance, at δ 23.0 ppm (in $CDCl_3$) in agreement with the *trans*-configuration. *trans*-$[PdIR(PPh_3)_2]$, R = (2) underwent smooth metathesis to *trans*-$[Pd(SCN)R(PPh_3)_2]$ when treated with potassium thiocyanate. The IR spectrum of this thiocyanate complex was almost identical to that of the iodide except for a very strong absorption at 2070 cm^{-1} (Nujol) due to $\nu(C{\equiv}N)$.

Platinum complexes *trans*-$[PtIR(PPh_3)_2]$, R = 3,4-dimethoxyphenyl, (2), (3) or (4) were made by the oxidative addition of the corresponding aryl iodide to $[Pt(\textit{trans}\text{-stilbene})(PPh_3)_2]$ [8] in benzene. Microanalytical data for these arylplatinum(II) complexes are given in Table 1. In the ^1H NMR spectra of the crown ether complexes (in $CDCl_3$) the crown ether methylene hydrogens absorb at δ 3.0—4.5 ppm as unresolved multiplets. The three aryl hydrogens H_a, H_b, and H_c for *trans*-$[PtIR(PPh_3)_2]$, R = (2) absorb as follows: H_a singlet at δ 5.9 ppm with Pt-satellites, $^3J(PtH_a)$ 57 Hz; H_b a broad central doublet at δ 6.34 ppm, $^3J(H_b—H_c)$ 7 Hz with satellites $^3J(PtH_b)$ 60 Hz and H_c a doublet at δ 5.96 ppm with $^3J(H_c—H_b)$ 7 Hz for which the satellites are obscured. The ^1H NMR parameters for H_a, H_b and H_c for R = (3) or 3,4-dimethoxyphenyl (5) were the same as for R = (2) within experimental error. For the 3,4-dimethoxyphenyl complex

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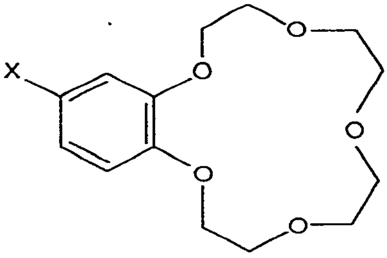
* This is the nomenclature adopted by Chemical Abstracts for crown ethers.



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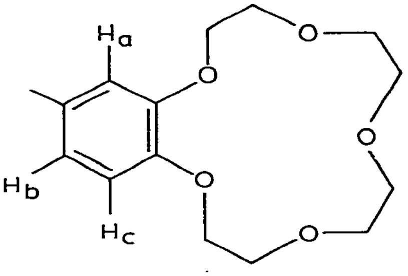

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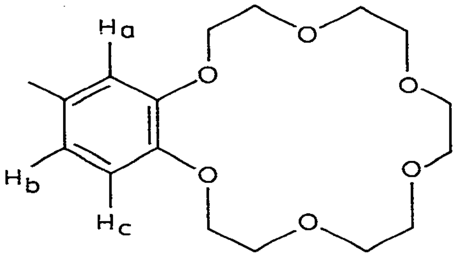

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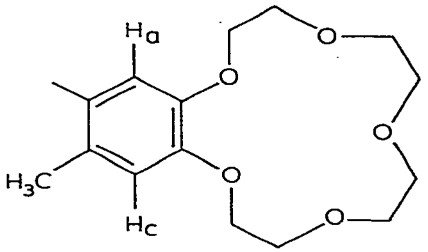

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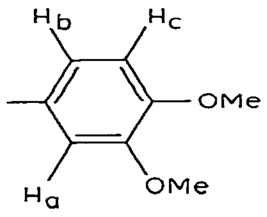

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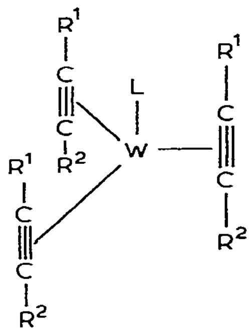

(6)

the methoxyl hydrogens absorb at δ 3.08 and 3.52 ppm. For the methyl-substituted crown complex *trans*-[PtIR(PPh$_3$)$_2$], R = (4) the methyl group absorbs at δ 6.41 ppm, ^3J(PtH) 64 Hz and H$_c$ at δ 5.82 ppm, ^3J(PtH) 16 Hz. The ^{31}P NMR spectra for the four complexes *trans*-[PtIR(PPh$_3$)$_2$] in 1/1 CDCl$_3$/CH$_3$COCH$_3$ solution all show single peaks with Pt-satellites, the δ {^1J(PtP)} values are (2) 21.7 ppm, 3062 Hz; (3) 21.2 ppm, 3073 Hz; (4) 20.45 ppm, 3067 Hz; (5) 21.3 ppm, 3078 Hz. On adding one mol of sodium iodide per platinum atom to each of the solutions the δ-values did not change appreciably but values of ^1J(PtP) decreased by 29—35 Hz for the three crown complexes with R = (2), (3) or (4) whereas for the model complex, R = (5) the value of ^1J(PtP) did not change. Further additions of sodium iodide above one mol per platinum atom caused

TABLE 1

COLOUR, MELTING POINT, ANALYTICAL AND MOLECULAR WEIGHT DATA FOR SOME SUBSTITUTED CROWN ETHERS, ORGANO-TRANSITION METAL COMPOUNDS CONTAINING CROWN ETHER MOIETIES, AND SOME ANALOGOUS COMPOUNDS CONTAINING 3,4-DIMETHOXYPHENYL GROUPS

Compound	Colour	M.p. (°C)	Analytical data (found (calcd.) (%))			Mol. wt. [a]
			C	H	Hal [N]	
1, X = CH=CHCOOH	White	194	60.35 (60.35)	6.35 (6.55)		
1, X = CH=CHCOOMe	White	80—83	61.35 (61.35)	7.05 (6.9)		
1, X = CH=CHCOOEt	White	98—99	61.9 (62.3)	6.9 (7.15)		
1, X = CH=CHCOCl	White	[b]	57.5 (57.2)	6.1 (5.9)		
1, X = C≡CPh	White	105—108	71.55 (71.7)	6.65 (6.6)		
$PhC\equiv CC_6H_3(OMe)_2$-3,4	White	94—95	80.65 (80.95)	5.95 (5.8)		
trans-$[PdIR(PPh_3)_2]$, R = (2)	Buff	134—145	58.5 (58.6)	5.05 (4.8)	13.2 (12.4)	
trans-$[PdIR(PPh_3)_2]$, R = (3)	Buff	85—89	58.7 (58.4)	5.1 (5.0)	11.5 (11.9)	1043 (1069)
trans-$[Pd(SCN)R(PPh_3)_2]$, R = (2)	Buff	146—150 [c]	64.05 (64.05)	5.1 (5.15)		
trans-$[PtIR(PPh_3)_2]$ R = (2)	Buff	164—167 [c]	53.85 (53.9)	4.45 (4.45)	11.25 (11.4)	1111 (1114)
trans-$[PtIR(PPh_3)_2]$ R = (3)	Buff	143—146	53.7 (53.9)	4.6 (4.6)	10.85 (10.95)	1176 (1157)
trans-$[PtIR(PPh_3)_2]$ R = (4)	Buff	160—162	54.05 (54.3)	4.45 (4.55)	11.1 (11.25)	
trans-$[PtI\{C_6H_3(OMe)_2\text{-}3,4\}(PPh_3)_2]$	Buff	220—226 [c]	54.1 (53.7)	3.7 (4.0)	12.5 (12.9)	
trans-$[PtClR(PPh_3)_2]$, R = (2)	White	220—222 [c]	58.2 (58.7)	4.6 (4.8)	4.0 (3.45)	
trans-$[Pt(SCN)R(PPh_3)_2]$, R = (2)	White	214—216 [c]	58.95 (58.6)	4.8 (4.75)		1061 (1045)
trans-$[PtCl(COR)(PPh_3)_2]$, R = (2)	White	151—153	58.65 (59.1)	4.7 (4.8)		
$[Pt(PPh_3)_2\{PhC\equiv CC_6H_3(OMe)\text{-}3,4\}]$	Cream	[b]	65.5 (65.2)	4.7 (4.6)		
$[Co_2(CO)_6(PhC\equiv CR)]$, R = (2)	Brown	87—89	51.8 (51.4)	3.8 (3.7)		
$[Co_2(CO)_6\{PhC\equiv CC_6H_3(OMe)_2\text{-}3,4\}]$	Brown	89—91	50.05 (50.4)	2.7 (2.7)		
$[Ni_2(C_5H_5)_2(PhC\equiv CR)]$, R = (2)	Dark green	120—122	61.9 (62.4)	5.7 (5.55)		
$[Ni_2(C_5H_5)_2\{PhC\equiv CC_6H_3\text{-}(OMe)_2\text{-}3,4\}]$	Dark green	132—134	63.85 (64.25)	4.95 (4.95)		
$[W(CO)(PhC\equiv CR)_3]$, R = (2)	Dark yellow	173—174 [c]	61.35 (61.1)	5.5 (5.5)		1289 (1317)
$[W(CO)\{PhC\equiv CC_6H_3(OMe)_2\text{-}3,4\}_3]$	Yellow	104—105	63.2 (63.5)	4.5 (4.6)		897 (926)
$[W(PMe_2Ph)\{PhC\equiv CC_6H_3\text{-}(OMe)_2\text{-}3,4\}_3]$	White	184—186 [c]	65.3 (64.9)	5.05 (5.15)		1037 (1036)
$[Cr(CO)_3\{$benzo-15-crown-5$\}]$	Yellow	120—122	50.35 (50.5)	4.85 (4.95)		

continued

TABLE 1 Continued

Compound	Colour	M.p. (°C)	Analytical data (found (calcd.) %))			Mol. wt. [a]
			C	H	Hal [N]	
[Cr(CO)$_3${benzo-18-crown-6}]	Yellow	95—96	51.4	5.45		
			(50.9)	(5.4)		
[Cr(CO)$_3${15-methyl-[benzo-15-crown-5]}]	Yellow	119—122	51.5	5.3		
			(51.65)	(5.3)		
[Cr(CO)$_3${C$_6$H$_4$(OMe)$_2$-1,2}]	Yellow	105—107	48.4	3.7		
			(48.2)	(3.7)		
[Cr(CO)$_3${benzo-15-crown-5}Na]SCN	Green	135—138	44.0	4.05	[3.35	
			(44.5)	(4.15)	(2.9)]	

[a] Determined on a Hitachi—Perkin—Elmer apparatus Model 115 in benzene. [b] Decomposes without melting. [c] With decomposition.

no further changes in ^1J(PtP) values for the crown complexes. These results suggest that a 1/1 interaction between sodium iodide and the crown platinum complex is occurring.

The substituted benzo-15-crown-5 complex iodide, *trans*-[PtIR(PPh$_3$)$_2$]R = (2) reacts with silver nitrate in acetone to give the corresponding nitrate as an unstable white solid. This was not characterized but converted to the chloride by treatment with an excess of lithium chloride in acetone. *trans*-[PtClR(PPh$_3$)$_2$] shows a very similar IR spectrum to that of the corresponding iodide except for a strong band at 280 cm^{-1} due to ν(Pt—Cl) (in Nujol). The ^{1}H NMR spectrum is almost identical to that of the corresponding iodide and the ^{31}P NMR spectrum (CDCl$_3$) consists of one peak at δ 24.15 ppm with satellites ^1J(PtP) 3128 Hz. *trans*-[PtIR(PPh$_3$)$_2$] react readily with KSCN in acetone to give the corresponding thiocyanate *trans*-[Pt(SCN)R(PPh$_3$)$_2$], R = (2), for which ν(C≡N) 2080 cm^{-1} (Nujol).

We have also studied reactions of the new acetylene crown ether PhC≡CR, R = (2) and the model compound PhC≡CC$_6$H$_3$(OMe)$_2$-3,4 with some transition metal compounds. These two new acetylenes were prepared by treating copper phenylacetylide with the iodide (1, X = I) or 3,4-dimethoxyiodobenzene (see Experimental) and ref. 9. The crown ether acetylene showed a molecular ion of the expected value of *m/e* 368. Platinum—acetylene complexes of the type [Pt(ac)(PPh$_3$)$_2$], ac = PhC≡CC$_6$H$_3$(OMe)$_2$-3,4 and PhC≡CR, R = (2) were prepared by a general method [10] viz. the hydrazine reduction of *cis*-[PtCl$_2$(PPh$_3$)$_2$] in the presence of the acetylene. Both complexes are cream-coloured solids but the crown ether complex [Pt(PhC≡CR)(PPh$_3$)$_2$] decomposed on attempted recrystallization and consistent microanalytical data could not be obtained. Both complexes showed an IR absorption band at 1745 cm^{-1} due to ν(C≡C) lowered by complexation, consistent with literature values for similar compounds [11]. The ^{31}P NMR spectra for the two complexes were virtually identical (in C$_6$D$_6$/C$_6$H$_6$) and the chemical shifts and coupling constants for the non-equivalent phosphorus nuclei (P$_A$ and P$_B$) the same for the two complexes. δ(P$_A$) 28.6 ppm, δ(P$_B$) 27.6 ppm. ^1J(PtP$_A$) 3452 Hz, ^1J(PtP$_B$) 3436 Hz and ^2J(P$_A$P$_B$) 33 Hz.

Acetylenes can bridge two metal atoms and to demonstrate that one could do this with the crown acetylene we have prepared the complexes $[Co_2(CO)_6(ac)]$ [12] and $[Ni_2(C_5H_5)_2(ac)]$ [13,14] with ac = $PhC{\equiv}CR$, R = (2). We have also prepared similar complexes with $PhC{\equiv}CC_6H_3(OMe)$-3,4. Microanalytical data are given in Table 1. Both the cobalt compounds show six IR absorption bands between 2000 and 2100 cm^{-1} due to $\nu(C{\equiv}O)$ and the ^1H NMR spectra are in agreement with the assigned structures. The complex $[Co_2(CO)_6\{PhC{\equiv}CC_6H_3(OMe)_2\text{-}3,4\}]$ is sufficiently volatile to give a mass spectrum with a molecular ion peak at *m/e* 524, as expected, and a base peak at *m/e* 440 corresponding to loss of 3 CO groups. A mass spectrum could not be obtained for the analogous crown ether complex.

The complexes $[Ni_2(C_5H_5)_2\{PhC{\equiv}CR\}]$, R = (2) or $C_6H_3(OMe)_2$-3,4 were prepared by the general method from nickelocene [13,14]. Both complexes are very dark crystalline solids, soluble in light petroleum, to give green solutions. Both show a medium strength IR absorption band at 1620 cm^{-1}, tentatively assigned as $\nu(C{\equiv}C)$. The ^1H NMR spectra (60 MHz) of both complexes show complex multiplets δ 6.8—7.5 ppm together with a singlet at δ 5.25 ppm due to the cyclopentadienyl protons. The crown ether complex shows a multiplet δ 3.5 to 4.5 ppm due to the crown ether methylene protons and $[Ni_2(C_5H_5)_2\{PhC{\equiv}CC_6H_3(OMe)_2\text{-}3,4\}]$ a peak at δ 3.76 ppm corresponding to the methoxyl protons. This complex also gave a mass spectrum with a molecular ion pattern consisting of nine peaks *m/e* 484 to 492 with the most intense at *m/e* 486 as expected. Nickel has five isotopes and the distribution pattern of this molecular ion corresponded well with theory. A mass spectrum could not be obtained for the substituted crown ether complex.

Some of the most unusual transition metal—acetylene complexes are of the type $[W(CO)(ac)_3]$. We have investigated the possibility of forming such a complex with the crown acetylene $PhC{\equiv}CR$, R = (2) and also the model $PhC{\equiv}CC_6H_3(OMe)_2$-3,4. Both the complexes were prepared readily by the general method [15,16] as orange, crystalline solids soluble in common organic solvents. The IR spectra of both complexes (in Nujol) show a very strong sharp peak at 2060 cm^{-1} due to $\nu(C{\equiv}O)$ and a broad medium strength band between 1660 and 1670 cm^{-1}, assigned as $\nu(C{\equiv}C)$. These values agree with literature values for analogous complexes [15]. The ^1H NMR spectrum of the "model" complex, $W(CO)\{PhC{\equiv}CC_6H_3(OMe)_2\text{-}3,4\}_3$ showed a broad multiplet δ 6.5—7.6 ppm corresponding to the aromatic protons and four singlets at δ 3.37, 3.42, 3.72, and 3.83 ppm with intensity ratios approximately 1/1/1/3 corresponding to the methoxy protons. This suggests that a mixture of isomers was present in solution in which the 3,4-methoxyphenyl groups (R^1 or R^2 in (6)) could be pointing towards or pointing away from the carbonyl group (L = CO in (6)). The ^1H NMR pattern of the crown ether complex was complicated with a broad multiplet at δ 6.5—7.6 ppm (aromatic protons) and another δ 3.5—4.5 ppm (crown ether methylene protons).

PMe_2Ph displaced carbon monoxide from both complexes $W(CO)(PhC{\equiv}CR)_3$ to give $W(PMe_2Ph)(PhC{\equiv}CR)_3$. The complex with R = $C_6H_3(OMe)_2$-3,4 shows a medium strength IR absorption band at 1650 cm^{-1} due to $\nu(C{\equiv}C)$ and the ^1H NMR spectrum a broad doublet at δ 1.78 ppm, $^2J(PH)$ 8 Hz for the PMe_2Ph methyl protons and two methoxyl peaks (δ 3.30 and 3.74 ppm). The ^{31}P NMR spectrum (in C_6D_6/C_6H_6) showed two peaks (δ 5.17 and 5.23 ppm) each with satellites due to ^{183}W (14.4% abundance) $^1J(^{183}W—P)$ 134 Hz. This indicates the presence of isomers (6) with R^1 and R^2 either Ph or $C_6H_3(OMe)_2$-3,4. The cream-coloured microcrystalline crown ether complex $W(PMe_2Ph)(PhC{\equiv}CR)_3$, R = (2) was less stable than the model and could not be isolated analytically pure. It showed an IR absorption at ca. 1645 cm^{-1} due to ν(C≡C). The ^1H NMR spectrum was poor due to decomposition and broadening of the multiplets and although two ^{31}P resonances (at δ 4.97 and 5.03 ppm) could be observed the spectrum was very poor due to decomposition in solution and the satellites could not be observed.

We have also treated the crown aldehyde (1, X = CHO) [7] with malonic acid in the presence of pyridine/piperidine to give the substituted acrylic acid (1, X = CH=CHCOOH) (Knovenagel condensation). This acid was converted into the methyl ester (1, X = CH=CHCOOMe) by treatment with diazomethane, into the ethyl ester (1, X = CH=CHCOOEt) by treatment with ethanol/sulphuric acid, and into the acyl chloride (1, X = CH=CHCOCl) by treatment with thionyl chloride.

The acyl chloride (1, X = CH=CHCOCl) reacted with the platinum(0) complex $[Pt(stilbene)(PPh_3)_2]$, effecting oxidative addition and displacement of stilbene to give the acylplatinum(II) complex *trans*-$[PtCl(COR)(PPh_3)_2]$ in 90% yield. This compound had ν(Pt—Cl) 256 cm^{-1} and ν(C=O) 1599 cm^{-1} in its IR spectrum (Nujol), and the ^{31}P NMR spectrum (C_6H_6) showed a singlet with satellites δ 20.9 ppm, ^1J(PtP) 3321 Hz. The ^1H NMR spectrum ($CDCl_3$) was complex but showed the expected relative areas in the integrated spectrum.

The olefinic ester derivative of benzo-15-crown-5 (1, X = CH=CHCOOEt) is an electronegative olefin and therefore one would expect it to form olefin—platinum(0) complexes of the type $[Pt(olefin)(PPh_3)_2]$ [8]. It reacted with $[Pt(C_2H_4)(PPh_3)_2]$ in benzene with evolution of ethylene and although the desired complex was formed and obtained in good yield as a microcrystalline yellow solid, m.p. 84—87 from chloroform/light petroleum, ^{31}P NMR spectroscopy showed it to contain an impurity (probably Ph_3PO) which we could not remove. The ^{31}P NMR data ($CDCl_3$) for the complex are $\delta(P_A) = \delta(P_B) = 29.4$ ppm. $^1J(PtP_A)$ 4192 Hz, $^1J(PtP_B)$ 3633 Hz, $J(P_AP_B)$ 46 Hz and are similar to those of the model complex $[Pt\{EtOOCCH{=}CHC_6H_3(OMe)_2\text{-}3,4\}(PPh_3)_2]$ for which $\delta(P_A) = \delta(P_B) = 29.1$ ppm, $^1J(PtP_A)$ 4190 Hz, $^1J(PtP_B)$ 3628 Hz, $J(P_AP_B)$ 46 Hz. Both complexes i.e. crown and 3,4-dimethoxyphenyl derivative had ν(C=O) 1682 cm^{-1} (in Nujol). The model complex was obtained pure and gave good microanalytical results (Table 1).

We have also attempted to prepare benzo-substituted crown ether containing a Group VIA metal tricarbonyl group bonded to the arene ring. Mono- and bis-$Cr(CO)_3$ derivatives of dibenzo-18-crown-6 have been prepared by the UV irradiation of a mixture of dibenzo-18-crown-6 and $Cr(CO)_6$ in a 1/1 mixture of THF and isooctane [17]. We found this method gave a very poor yield with benzo-15-crown-5. However, when a mixture of benzo-15-crown-5 and $Cr(CO)_6$ was heated in THF/isooctane for ten days without irradiation at 24% yield of the required derivative $[Cr(CO)_3\{benzo\text{-}15\text{-}crown\text{-}5\}]$ was obtained. Similarly $[Cr(CO)_3(RH)]$, R = (3), (4) or (6) were prepared. All four complexes gave good mass spectra, in each case the base peak being the molecular ion. Peaks due to loss of one, two or three CO groups were also observed.

We have studied the action of sodium thiocyanate on [$Cr(CO)_3$(benzo-15-crown-5)] to see if the coordinating function of the crown ether moiety is present. When sodium thiocyanate and the tricarbonyl complex were heated in ethanol a green crystalline adduct [$Cr(CO)_3$(benzo-15-crown-5)NaSCN] m.p. 135—138°C was formed, see Table 1 for microanalytical data. This adduct was insoluble in common organic solvents and reacted with water to give back [$Cr(CO)_3$(benzo-15-crown-5)]. The IR absorption spectrum of the NaSCN adduct (Nujol mull) showed three strong bands assigned to $\nu(C\equiv O)$, 1950, 1865, and 1853 cm^{-1} and three due to $\nu(C\equiv N)$ 1088, 1059, and 2048 cm^{-1}. Free NaSCN absorbs at 2053 cm^{-1}.

Experimental

The general techniques and instruments were the same as those used previously [18]. Colours, melting points and microanalytical weight data are given in Table 1. IR spectra were measured in Nujol mulls. NMR spectra were measured in deuterochloroform unless stated otherwise. ^{31}P shifts are relative to 85% H_3PO_4. Spectroscopic data for the complexes is given in the discussion.

(1, X = CH=CHCOOH). A mixture of the crown aldehyde (1, X = CHO) (25.0 g, 0.084 mol) and malonic acid (17.6 g, 0.17 mol) was warmed with pyridine (100 cm^3) until it dissolved. Piperidine (4 cm^3) was added and the mixture heated at 80—90°C for 1 h then 110°C for 20 h. It was then cooled, water (100 cm^3) added followed by concentrated hydrochloric acid (120 cm^3) portionwise. The required product precipitated and was recrystallized from propan-2-ol. Yield 22.5 g, 80%. $\nu(C=O)$ 1701, 1672 cm^{-1}; $\nu(C=C)$ 1640 cm^{-1}.

(1, X = CH=CHCOOMe). The above acid (4.0 g, 0.0118 mol) in THF (15 cm^3) was treated with an excess of diazomethane in ether. The resultant yellow solution was evaporated to low bulk and the product isolated with propan-2-ol/light petroleum (b.p. 60—80°C). White microcrystals (3.1 g, 75%) $\nu(C=O)$ 1703 cm^{-1}, $\nu(C=C)$ 1618 cm^{-1}.

(1, X = CH=CHCOOEt). The above acid (12.4 g) was heated under reflux with ethanol (120 cm^3) containing concentrated sulphuric acid (6 cm^3) for 18 h. The mixture was cooled, poured into water and the product isolated with chloroform. Evaporation of the chloroform under reduced pressure and addition of hexane gave the required product which was purified by recrystallization from propan-2-ol/light petroleum (b.p. 60—80°C). Yield 12.0 g (90%) $\nu(C=O)$ 1710 cm^{-1}, $\nu(C=C)$ 1630 cm^{-1}.

(1, X = CH=CHCOCl). The crown acid (3.0 g, 8.9 mmol) was heated under reflux with thionyl chloride (12 cm^3) until effervescence ceased (1 h). The excess of thionyl chloride was removed under reduced pressure to give the required product as a pale yellow solid. A portion was recrystallized from toluene for analysis. Yield 3.0 (91%). $\nu(C=O)$ = 1762; $\nu(C=C)$ = 1672 cm^{-1}.

(1, X = C≡CPh). 15-Iodobenzo-15-crown-5 (1, X = I) (12.5 g, 31.6 mmol) in dry pyridine (150 cm^3) was heated with copper phenylacetylide (5.2 g, 31.6 mmol) at 120°C with stirring for 19 h. The resultant mixture was cooled, added to water (750 cm^3) and the product isolated with diethyl ether. The ether extracts were washed with dilute hydrochloric acid (100 cm^3), saturated sodium bicar-

bonate solution (100 cm^3) and water (100 cm^3). Removal of the ether gave the product 8.7 g, 23.6 mmol, 75%. $\nu(C{\equiv}C)$ 2200 cm^{-1}.

1,2-Dimethoxy-4-phenylethynylbenzene. This was prepared in a similar manner, as hexagonal plates from methanol. Yield 78%.

trans-[PdIR(PPh$_3$)$_2$], R = (2). 15-Iodobenzo-15-crown-5 (70 mg, 0.18 mmol) was added to a solution of $Pd(PPh_3)_4$ (0.20 g, 0.17 mmol) in benzene (10 cm^3). After 1 h at ca. 20°C the solvent was removed under reduced pressure, diethyl ether (10 cm^3) added and the product isolated as prisms and recrystallized from dichloromethane/hexane. Yield 0.16 g, 0.15 mmol, 83%.

trans-[PdIR(PPh$_3$)$_2$], R = (3) was prepared in a similar manner.

trans-[Pd(SCN)R(PPh$_3$)$_2$], R = (2). A mixture of the iodo complex described above (0.10 g, 0.097 mmol) and potassium thiocyanate (0.09 g, 0.97 mmol) in acetone (10 cm^3) was heated under reflux for 10 min, evaporated to dryness and water added. This gave the required product which formed needles from dichloromethane/methanol. Yield 68 mg, 0.071 mmol, 73%.

trans-[PtIR(PPh$_3$)$_2$], R = (2). A mixture of *trans*-stilbenebis(triphenylphosphine)platinum(0) (0.60 g, 0.66 mmol) and 15-iodobenzo-15-crown-5 (0.32 g, 0.80 mmol) in benzene (10 cm^3) was heated to ca. 70°C for 15 min. The solvent was removed under reduced pressure to give a red oil, which gave the required product when triturated with light petroleum (b.p. 60—80°C). It formed pale yellow prisms from dichloromethane/heptene. Yield 0.31 g, 0.27 mmol, 41%.

trans-[PtIR(PPh$_3$)$_2$] with R = (3) and (4); and trans-(3,4-dimethoxyphenyl)-iodobis(triphenylphosphine)platinum(II). These compounds were made in a similar manner in yields of 89, 46 and 72% respectively.

trans-[PtClR(PPh$_3$)$_2$], R = (2). Silver nitrate (90 mg, 0.55 mol) was added to a solution of the iodo complex (2, X = I, M = Pt, 0.31 g, 0.27 mmol) in acetone (10 cm^3). This mixture was then heated under reflux for 5 min, filtered, the solvent evaporated under reduced pressure and water (10 cm^3) added to the residue to give a white precipitate. This was collected, dissolved in acetone (10 cm^3) and lithium chloride (0.11 g, 2.7 mmol) added. The mixture was heated under reflux for 1 h, evaporated to dryness and water added. The resultant solid was recrystallized from dichloromethane/hexane. White needles (0.20 g, 0.20 mmol, 36%).

trans-[Pt(SCN)R(PPh$_3$)$_2$], R = (2). This was prepared in a similar manner to the palladium analogue. Yield 78%.

trans-[PtCl(COR)(PPh$_3$)$_2$], R = (2). A mixture of the crown acid chloride (1, X = CH=CHCOCl, 0.45 g, 1.26 mmol) and (stilbene)bis(triphenylphosphine)-platinum(0) (1.03 g, 1.14 mmol) in dry, degassed benzene (25 cm^3) was stirred with warming to ca. 50°C for 1 h. The small amount of precipitate was filtered off and the filtrate evaporated. The residual oil was triturated with hexane and the resultant solid recrystallized from chloroform/diethyl ether. Pale yellow microcrystals. Yield 1.0 g.

η^2-{1,2-Dimethoxy(4-phenylethynyl)benzene}bis(triphenylphosphine)platinum(0). Hydrazine hydrate (0.25 cm^3) was added to a suspension of *cis*-dichlorobis(triphenylphosphine)platinum(II) (0.22 g, 0.30 mmol) in ethanol (5 cm^3). The mixture was warmed to give a yellow solution. 1,2-Dimethoxy-(4-phenylethynyl)benzene (70 mg, 0.30 mol) was then added and the mixture

heated to ca. 60°C for 5 min. When cooled the required product separated as cream prisms, which were recrystallized from benzene/ethanol.

$\mathrm{Pt(PhC{\equiv}CR)(PPh_3)_2}$, R = (2). This was prepared in a similar manner but satisfactory microanalytical data could not be obtained, see Discussion.

$\mathrm{[Co_2(CO)_6(PhC{\equiv}CR)]}$, R = (2). The crown acetylene (1, X = C≡CPh) (1.34 g, 3.63 mmol) was added to a solution of dicobalt octacarbonyl (1.24 g, 3.63 mmol) in pentane (10 cm^3). The mixture was then stirred at ca. 20°C for 5 h. A heavy brown precipitate of the required complex formed and gave brown prisms from light petroleum (b.p. 40—60°C). Yield 1.99 g, 3.04 mol, 84%.

$\mathrm{[Co_2(CO)_6\{PhC{\equiv}CC_6H_3(OMe)\text{-}3,4\}]}$. This was prepared in a similar manner. Yield 87%.

$\mathrm{[Ni_2(\eta^5\text{-}C_5H_5)_2(PhC{\equiv}CR)]}$, R = (2). A mixture of the crown acetylene (1, X = C≡CPh) (0.87 g, 2.35 mmol) and nickelocene (0.89 g, 4.7 mmol) in toluene (25 cm^3) was heated under reflux for 18 h. The solvent was removed under reduced pressure and the resultant dark green gum extracted with light petroleum (b.p. 60—80°C) to give the product which formed dark green microcrystals from light petroleum (b.p. 60—80°C). Yield 1.03 g, 1.67 mmol, 70%.

$\mathrm{[Ni_2(\eta^5\text{-}C_5H_5)_2\{PhC{\equiv}CC_6H_3(OMe)\text{-}3,4\}]}$. This was prepared similarly. Yield 48%.

$\mathrm{[W(CO)(PhC{\equiv}CR)_3]}$, R = (2). A mixture of tungsten hexacarbonyl (0.33 g, 0.93 mmol) and the crown acetylene (1, X = C≡CPh) (1.02 g, 2.78 mmol) was heated under reflux in acetonitrile (12 cm^3) for 40 h. The resultant yellow solution was cooled and ethanol (20 cm^3) added. This gave the required product which formed dark yellow microcrystals from ethanol. Yield (0.89 g, 0.67 mmol, 73%).

$\mathrm{[W(CO)\{PhC{\equiv}CC_6H_3(OMe)_2\text{-}3,4\}_3]}$. This was prepared similarly. Yield 85%.

$\mathrm{[W(PMe_2Ph)\{PhC{\equiv}CC_6H_3(OMe)_2\text{-}3,4\}_3]}$. Dimethylphenylphosphine (0.083 g, 0.60 mmol) was added to a solution of the carbonyl complex $\mathrm{[W(CO)\{PhC{\equiv}CC_6H_3(OMe)_2\text{-}3,4\}_3]}$ (0.27 g, 0.29 mmol) in benzene (10 cm^3) and the mixture heated under reflux for 20 h. The resultant solution was filtered through florisil, the solvent removed under reduced pressure and the residue recrystallized from benzene/hexane. White microcrystals (0.22 g, 0.21 mmol, 74%).

$\mathrm{[Pt\{EtOOCCH{=}CHC_6H_3(OMe)_2\text{-}3,4\}(PPh_3)_2]}$. A mixture of $\mathrm{[Pt(C_2H_4)(PPh_3)_2]}$ (0.169 g, 0.266 mmol) and $\mathrm{EtOOCCH{=}CHC_6H_3(OMe)_2\text{-}3,4}$ (0.054 g, 0.27 mmol) was treated with dry, degassed benzene (5 cm^3) under argon. The solids dissolved with evolution of ethylene. Most of the benzene was removed under reduced pressure and light petroleum (b.p. 60—80°C) added. This gave the required complex as pale yellow microcrystals. Yield 65%.

$\mathrm{[Cr(CO)_3(benzo\text{-}15\text{-}crown\text{-}5)]}$. A mixture of chromium hexacarbonyl (5.19 g, 23.6 mmol) and benzo-15-crown-5 (6.33 g, 23.6 mmol) in isooctane (60 cm^3) was heated under reflux for 10 days. The solvent was removed under reduced pressure and methanol (10 cm^3) added to the residue. Unreacted chromium hexacarbonyl was removed by filtration and water (40 cm^3) added to the filtrate. The resultant yellow precipitate was recrystallized from propan-1-ol to give the required product as yellow rhombs. Yield 3.27 g, 8.09 mmol, 34%.

$\mathrm{[Cr(CO)_3(1,2\text{-}dimethoxybenzene)]}$, $\mathrm{[Cr(CO)_3(benzo\text{-}18\text{-}crown\text{-}6)]}$, and $\mathrm{[Cr(CO)_3(15\text{-}methylbenzo\text{-}15\text{-}crown\text{-}5)]}$. These compounds were prepared in a similar manner.

[Cr(CO)$_3$(benzo-15-crown-5)Na]SCN. A mixture of sodium thiocyanate (0.075 g, 0.92 mmol) and Cr(CO)$_3$(benzo-15-crown-5) (0.37 g, 0.92 mmol) in ethanol (10 ml) was heated until a solution formed. The mixture was put aside to cool to give the adduct as green needles (0.21 g, 0.43 mmol, 47%).

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