Synthesis of some phosphino- and arsinobenzenechromium tricarbonyl derivatives and metal carbonyl clusters

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Abstract: The synthesis of a number of new phosphino- and arsinobenzenechromium tricarbonyl ligands $ER_2C_6H_5Cr(CO)_3$ ($ER_2 = PEt_2$, PPr_2^i , PBu_2^i , PPh_2 , $AsPh_2 AsMe_2$), $ER[C_6H_5Cr(CO)_3]_2$ (ER = PEt, PBu^t , PPh, AsPh) has been achieved by reacting lithium derivatives of benzenechromium tricarbonyl with appropriate chlorophosphines or iodoarsines. The spectroscopic properties of these ligands are described. The structure of $Pr_2PC_6H_5Cr(CO)_3$ was determined by an X-ray crystallographic study. This is the first solid state structure to be reported for a phosphinobenzenechromium tricarbonyl derivative. The structures of four metal carbonyl cluster complexes were also determined. Crystals of $Pr_2PC_6H_5Cr(CO)_3$ ($3, C_{15}H_{19}CrO_3P$) are monoclinic, space group $P2_1/c$, a = 8.150(2) Å, b = 13.490(2) Å, c = 15.125(1) Å, $\beta = 100.19(1)^\circ$, Z = 4; those of $Ru_3(CO)_{11}[PPr_2C_6H_5Cr(CO)_3]$ ($15, C_{26}H_{19}CrO_{14}PRu_3$) are monoclinic, space group $P2_1/n$, a = 8.565(2) Å, b = 21.808(3) Å, c = 17.167(3) Å, $\beta = 97.41(2)^\circ$, Z = 4; those of $Ru_3(CO)_{10}[PPh_2C_6H_5Cr(CO)_3]_2$ ($19, C_{32}H_{15}CrO_{14}PRu_3$) are orthorhombic, space group Pbca, a = 17.367(4) Å, b = 24.471(5) Å, c = 16.096(3) Å, Z = 8; those of $Ru_3(CO)_{10}[PPr_2C_6H_5Cr(CO)_3]_2$ ($19, C_{32}H_{15}CrO_{14}PRu_3$) are orthorhombic, space group Pbca, a = 17.367(4) Å, b = 24.471(5) Å, c = 16.096(3) Å, Z = 8; those of $Ru_3(CO)_{10}[PPr_2C_6H_5Cr(CO)_3]_2$. ($16, C_{40}H_{38}Cr_2O_{16}P_2Ru_3$ ·Cr4_2Cl₂) are orthorhombic, space group $P2_1/2$, a = 13.832(3) Å, b = 17.558(2) Å, c = 10.144(1) Å, Z = 2; and those of $Os_3(CO)_9[PEt_2C_6H_5Cr(CO)_3]_3$ ($26, C_{48}H_{45}Cr_3O_{18}Os_3P_3$) are trigonal, space group $P\overline{3}$, a = 15.7558(4) Å, c = 12.662(1) Å, Z = 2. The structures were solved by the Patterson method and were refined by full-matrix least-squares procedures to R = 0.031, 0.027, 0.029, 0.025, and 0.029 ($R_w = 0.027, 0.024, 0.024, 0.023,$ and

Key words: metal carbonyl clusters, phosphinobenzenechromium tricarbonyl derivatives, arsinobenzenechromium tricarbonyl derivatives, crystal structures.

Résumé : On a synthétisé un certain nombre de nouveaux ligands, les phospino et arsinobenzène chrome tricarbonyle $ER_2C_6H_5Cr(CO)_3$ ($ER_2 = PEt_2$, PPr^i_2 , PBu'_2 , PPh_2 , $AsPh_2$, $AsPh_2$, $AsMe_2$), $Er[C_6H_5Cr(CO)_3]_2$, ($ER = PEt_2$, PBu'_2 , PPh_2 , $AsPh_2$), $AsPh_2$, $AsMe_2$), $Er[C_6H_5Cr(CO)_3]_2$, $ER = PEt_2$, PPh_2 , $AsPh_2$, $AsPh_2$, $AsMe_2$), $Er[C_6H_5Cr(CO)_3]_2$, $ER = PEt_2$, PPh_2 , $AsPh_2$, $AsPh_2$, $AsMe_2$), $Er[C_6H_5Cr(CO)_3]_2$, $ER = PEt_2$, PPh_2 , $AsPh_2$, $AsPh_2$, $AsMe_2$), $Er[C_6H_5Cr(CO)_3]_2$, $ER = PEt_2$, PPh_2 , $AsPh_2$, $AsPh_2$, $AsMe_2$), $Er[C_6H_5Cr(CO)_3]_2$, $ER = PEt_2$, PPh_2 , $AsPh_2$, $AsPh_2$, $AsMe_2$), $Er[C_6H_5Cr(CO)_3]_2$, $ER = PEt_2$, PPh_2 , $AsPh_2$, $AsPh_2$, $AsMe_2$), $Er[C_6H_5Cr(CO)_3]_2$, $ER = PEt_2$, PPh_2 , $AsPh_2$, réagir des dérivés lithiés du benzène chrome tricarbonyle avec les chlorophosphines ou les iodoarsines appropriés. On décrit les propriétés spectroscopiques de ces ligands. On a déterminé, par cristallographie de rayons X, la structure du composé $Pr'_2PC_6H_5Cr(CO)_3$. Cette publication représente la première étude d'un dérivé phosphinobenzène chrome tricarbonyle dans l'état solide. On a également déterminé la structure des complexes de quatre agrégats de métal tricarbonyle. Les cristaux de $Pr_{2}^{\prime}C_{6}H_{5}Cr(CO)_{3}$ (3, $C_{13}H_{19}CrO_{3}P$) appartiennent au groupe d'espace monoclinique $P2_{1}/c$, avec a = 8,150(2) Å, b = 13,490(2) Å, c = 15,125(1) Å, $\beta = 100,19(1)^{\circ}, Z = 4$; les cristaux de Ru₃(CO)₁₁ [PPrⁱ₂C₆H₅Cr(CO)₃] (15, C₂₆H₁₉CrO₁₄PRu₃) appartiennent au groupe d'espace monoclinique P_2/n , avec a = 8,565(2) Å, b = 21,808(3) Å, c = 17,167(3) Å, $\beta = 97,41(2)^\circ$, Z = 4; les cristaux de $Ru_3(CO)_{10}[PPh_2C_6H_5Cr(CO)_3]_2$ (19, $C_{32}H_{15}CrO_{14}PRu_3$) appartiennent au groupe d'espace orthorhombique *Pbca*, avec *a* = 17,367(4) Å, b = 24,471(5) Å, c = 16,096(3) Å, Z = 8; les cristaux de Ru₃(CO)₁₀[PPr¹₂C₆H₅Cr(CO)₃]₂·C₂Cl₂ (16, $C_{40}H_{38}Cr_2O_{16}P_2Ru_3 \cdot CH_2Cl_2)$ appartiennent au groupe d'espace orthorhombique $P2_12_12_1$, avec a = 13,832(3) Å, b = 17,558(2) Å, c = 19,144(1) Å, Z = 2; et les cristaux de Os₃(CO)₉[PEt₂C₆H₅Cr(CO)₃]₃ (26, C₄₈H₄₅Cr₃O₁₈Os₃P₃) appartiennent au groupe d'espace trigonal $P\overline{3}$, avec a = 15,7558(4) Å, c = 12,662(1) Å, Z = 2. On a résolu les structures par la méthode de Patterson et on les a affinées par la méthode des moindres carrés, matrice complète, jusqu'à des valeurs de R = 0.031, 0.027, 0.029, 0.025 et $0,029 \ (R_w = 0,027, 0,024, 0,024, 0,023 \text{ et } 0,025)$ pour respectivement 2326, 4110, 3878, 3046 et 4093 réflexions avec $I \ge 3\sigma(I)$.

Mots clés : agrégats de métal carbonyle, dérivés phosphinobenzène chrome tricarbonyle, dérivés arsinobenzène chrome tricarbonyle, structures des cristaux.

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Introduction

The pyrolysis of metal cluster derivatives of arylphosphines and arsines has proved to be a fruitful procedure for the preparation of cluster-bound arynes such as benzyne, ferrocyne, and naphthyne (1–3). We have also described how similar reactions give rise to derivatives of benzynechromium tricarbonyl (4). The present paper is principally concerned with the preparation and characterization of some metal carbonyl derivatives of the type $M_3(CO)_{12-n}(ER_2Ar')_n$ (M = Ru, Os; E = As, P; R = alkyl, aryl; Ar' = (η^6 -C₆H₅)Cr(CO)₃; n = 1, 2) that have been used as precursors in the synthesis of aryne derivatives. We also describe the preparation of seven new phosphines and arsines containing the (η^6 -C₆H₅)Cr(CO)₃ moiety.

Experimental

Unless otherwise stated, all reactions and subsequent manipulations involving organometallic reagents were conducted under an argon atmosphere by using standard Schlenk and vacuum line techniques.

Phosphorus trichloride, chlorodiethylphosphine, dichloroethylphosphine, chlorodiphenylphosphine, and dichlorophenylphosphine were purchased from Strem Chemicals Inc. They were stored under argon after distillation under reduced pressure. The purity of all phosphines was ascertained by using ³¹P{¹H} NMR spectroscopy. Ruthenium trichloride (kindly loaned by Johnson Matthey Ltd.), *n*-butyllithium (Aldrich), chromium hexacarbonyl (Strem), and osmium carbonyl (Steck) were used as received.

Column chromatography was carried out by using silica gel (230–400 mesh) or neutral alumina (80–200 mesh, Brockman Activity I) obtained from BDH Co.

¹H NMR spectra were recorded on Varian XL-300 (299.94 MHz), Bruker WH-400 or a WH-200FT (400.00 MHz, or 200.00 MHz) spectrometers, and are referenced to CDCl₃ or CD₂Cl₂ set at 7.25 ppm, and 5.32 ppm, respectively, at ambient temperature. ³¹P{¹H} NMR spectra were recorded on Varian XL-300 (121.42 MHz) or Bruker WH-200 (80.96 MHz) spectrometers and are referenced to external PPh₃ (CDCl₃) set at -5.6 ppm relative to 85% H₃PO₄ (aq) unless otherwise indicated. All chemical shifts are reported in ppm and coupling constants in Hz.

Infrared spectra were recorded by using a Perkin–Elmer 598, 783 or 1710 FTIR spectrophotometer. The spectra were calibrated by using the 1601 cm^{-1} band of polystyrene.

Low-resolution electron impact (EI) mass spectra were obtained by using a Kratos/AEI MS902 mass spectrometer, which was operated in the direct insertion mode (70 eV, 120–150°C source temperature). Fast atom bombardment (FAB) mass spectra were measured using an updated MS-9 mass spectrometer equipped with a FAB source. The matrix was 3-nitrobenzyl alcohol.

The following reagents were prepared by literature methods: $C_6H_5Cr(CO)_3$ (5), $Ru_3(CO)_{12}$ (6), $Os_3(CO)_{11}(CH_3CN)$, $Os_3(CO)_{10}(CH_3CN)_2$ (7), $(CH_3)_2AsI$ (8), $Bu_2'PCI$ (9), $(CH_3CN)_3Cr(CO)_3$ (10), $Ru_3(CO)_{11}(CH_3CN)$ (11), $Na[(C_6H_5)_2CO]$ (~0.025 M in THF) (12).

Preparation of Bu⁴PCl₂

A freshly prepared Grignard solution of Bu'MgCl (2 M, 250 mL) was added dropwise with stirring to phosphorus trichlo-

Scheme 1. Key to compounds.

R ₂ EC ₆ H	[₅ Cr(CO)3	RE[C ₆]	H ₅ Cr(C	O) ₃] ₂
$R_2E =$	Ph₂P,	1	RE =	PhP,	7
	Bu ^r 2P,	2		Bu'P,	8
	Pr ⁱ ₂ P,	3		EtP,	9
	Et ₂ P,	4		PhAs,	10
	Me ₂ As,	5			
Ru ₃ (CO) ₁₁ L		Ru ₃ (C	O) ₁₀ L ₂	
L =	5,	11	L =	5,	12
	3,	15		3,	16
	1,	19		1,	20
	4,	22		4,	23
	7,	27			
	6,	29			
Os ₃ (CO) ₁₁ L		Os ₃ (C	O) ₁₀ L ₂	
L =	5,	13	L =	5,	14
	3,	17		3,	18
	1,	21		4,	25
	4,	24	Os ₃ (C	0) ₉ L ₃	
	7,	28	L =	4,	26

ride (68.5 g, 44 mL, 0.5 mol) dissolved in diethyl ether (200 mL) at -20° C: the temperature of the reaction mixture was then allowed to rise to room temperature. The mixture was refluxed for 1 h and then filtered to remove the white solid. Distillation of the filtrate under reduced pressure gave Bu'PCl₂ as a colorless liquid (35 g, 45%), which solidified on standing, bp 143–148°C (760 Torr; 1 Torr = 133.3 Pa). ³¹P{¹H} NMR (121.4 MHz, C₆D₆) δ : 199.9 (s). ¹H NMR (300 MHz, C₆D₆) δ : 1.0 (d).

Preparation of PrⁱPCl₂

A Grignard solution of PrⁱMgCl in ether (1.25 M, 800 mL) was added dropwise to a stirred diethyl ether solution of PCl₃ (55.0 g, 26 mL, 0.4 mol). A white precipitate formed during the addition and the reaction mixture was refluxed for an additional 2 h. The solution was separated from the precipitate by filtration through a medium porosity Schlenk filter. The ether solvent was removed by distillation at atmospheric pressure and the oily residue was distilled under reduced pressure. The product was an air-sensitive, colorless liquid (30 g, 65%), bp 27°C (3 mmHg). ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ : 139.2 (s). ¹H NMR (300 MHz, CDCl₃) δ : 1.80–1.91 (m, 2H), 1.05 (q, 6H).

Preparation of $[C_6H_5Cr(CO)_3]PBu_2^t$, 2

A solution of $C_6H_6Cr(CO)_3$ (1.0 g, 4.7 mmol) in THF (20 mL) in a Schlenk tube was cooled to $-78^{\circ}C$ and treated dropwise with *n*-BuLi in hexane (3.0 mL, 1.6 M, 4.8 mmol). The resulting solution was stirred at $-78^{\circ}C$ for 50 min, when Bu¹₂PCl (1.0 mL, 5.2 mmol) was added. The reaction mixture was stirred at $-78^{\circ}C$ for 1 h, warmed to room temperature, and stirred continuously for an additional hour. After evaporating the solvent in vacuo, the residual oil was dissolved in CH₂Cl₂ (20 mL) and then filtered under nitrogen through a frit packed with Celite to remove LiCl. The solvent was removed in vacuo to afford a red oil. Hexane (5 mL) was added to the red oil, the resultant suspension was stirred vigorously, and a yellow precipitate was obtained. The solid was further purified by recrystallization from hexane–CH₂Cl₂ (2/1) to yield **2** as a yellow crystalline solid: yield 80%. IR (KBr) ν (CO): 1960 (vs), 1900 (vs), 1880 (s), 1870 (sh), 1865 (s) cm⁻¹. ³¹P{¹H} NMR (121.42 MHz, CDCl₃) δ : 42.8 (s). ¹H NMR (300 MHz, CDCl₃) δ : 5.7 (t, J(H-H) = 6Hz, 2H), 5.6 (t, J(H–H) = 6 Hz, 1H), 5.2 (t, J(H– H) = 6 Hz, 2H), 1.2 (d, J(P–H) = 10 Hz, 18H). MS (EI) *m/e*: 358 [P⁺]. Anal. calcd. for C₁₇H₂₃CrO₃P: C 56.97, H, 6.47; found: C 56.80, H 6.52.

Preparation of [C₆H₅Cr(CO)₃]PPrⁱ₂, 3

Compound **3** was synthesized by the procedure described for the preparation of **2** except that Pr_2^iPCl (0.75 mL, 5.0 mmol) was used instead of Bu_2^iPCl . Yellow crystals of **3** were obtained after recrystallization from hexanes- CH_2Cl_2 (2:1) at $-30^{\circ}C$ (1.1 g, 70%). IR (KBr) ν (CO): 1970 (s), 1880 (s, br) cm⁻¹. ³¹P{¹H} NMR (121.42 MHz, CDCl₃) δ : 13.9 (s). ¹H NMR (300 MHz, CDCl₃) δ : 5.33 (t, J(H-H) = 5 Hz, 3H), 5.18 (t, J(H-H) = 5 Hz, 2H), 1.95 (q, 2H), 1.05 (dd, J(H-H) = 5.5Hz, 12H). MS (EI) *m/e*: 330 [P⁺]. Anal. calcd. for $C_{15}H_{19}CrO_3P$: C 54.55, H 5.76; found: C 54.72, H 5.87.

Preparation of [C₆H₅Cr(CO)₃]PEt₂, 4

Chlorodiethylphosphine (0.97 mL, 8.0 mmol) was similarly used to afford 4 as a red oil, which was ~90% pure according to its ³¹P NMR spectrum. ν (CO): 1978 (s), 1885 (s) cm⁻¹. ³¹P{¹H} NMR (121.42 MHz, CDCl₃) δ : -13 (s). ¹H NMR (300 MHz, CDCl₃) δ : 5.4 (t, J(H–H) = 6 Hz, 3H), 5.2 (t, J(H–H) = 6 Hz, 2H), 1.8 (q, 4H), 1.2 (m, 6H). IR (CH₂Cl₂) MS (EI) *m/e*: 302 [P⁺].

Preparation of $[C_6H_5Cr(CO)_3]$ AsMe₂, 5

A similar procedure was used to prepare **5** from Me₂AsI as a yellow solid (70% yield). IR (KBr) ν (CO): 1960 (s), 1880 (s, br) cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ : 1.4 (S, 6H), 5.5 (t, *J*(H–H) = 5.5 Hz, 3H), 5.3 (t, *J*(H–H) = 5.5 Hz, 2H). MS (EI) *m/e*: 318 [P⁺]. Anal. calcd. for C₁₁H₁₁AsCrO₃: C 41.53, H 3.49; found: C 41.63, H 3.49.

Preparation of [C₆H₅Cr(CO)₃]PPh₂, 1

A similar procedure was used to prepare 1 from Ph₂PCl as a yellow crystalline solid (85% yield). IR (KBr) ν (CO): 1980 (s), 1900 (s, br) cm⁻¹. ³¹P{¹H} NMR (121.42 MHz, CDCl₃) δ : -5.2 (s). ¹H NMR (300 MHz, CDCl₃) δ : 7.4 (br s, 10H), 5.4 (t, 1H), 5.2 (m, 4H). MS (EI) *m/e*: 398 [P⁺].

Preparation of $[C_6H_5Cr(CO)_3]_2AsPh_2$, 6

A similar procedure was used to synthesize **6** from Ph₂AsI as a yellow crystalline solid (80% yield). ¹H NMR (300 MHz, CDCl₃) δ : 7.4 (br s, 10H), 5.3 (br s, 1H), 5.2 (br s, 4H). MS (EI) *m/e*: 358 [P⁺]. Anal. calcd. for C₂₁H₁₅O₃AsCr: C 57.03, H 3.42. Found: C 56.74, H 3.21.

Preparation of [C₆H₅Cr(CO)₃]₂PBu^t, 8

Benzenechromium tricarbonyl (1.62 g, 7.55 mmol) was dissolved in THF (25 mL) at -78° C. A solution of *n*-butyllithium in hexane (4.8 mL, 1.6 M, 7.7 mmol) was added slowly with a syringe to the cold, stirred solution. The solution was then stirred at -78° C for 50 min. Cl₂PBu^t (0.65 g, 4 mmol) in THF (10 mL) was then added dropwise with a syringe to the solution. The reaction mixture was stirred at -78° C for an additional hour and allowed to warm to room temperature. The solvent was evaporated in vacuo. The residual red oil was dissolved in CH₂Cl₂ (20 mL) and then filtered through a short column of silica gel under nitrogen. Dark red impurities and LiCl were left on the top of the column. Evaporation of the eluate followed by crystallization of the solid residue from CH₂Cl₂-hexanes (1:2) afforded **8** (70% yield) as a yellow crystalline solid. IR (KBr) ν (CO): 1970 (s), 1890 (s, br) cm⁻¹. ³¹P{¹H} NMR (121.42 MHz, CDCl₃) δ : 20.7 (s). ¹H NMR (300 MHz, CDCl₃) δ : 5.7 (t, *J*(H–H) = 6 Hz, 2H), 5.4 (t, *J*(H–H) = 6 Hz, 4H), 5.2 (d, *J*(H–H) = 6 Hz, 4H). 1.2 (d, *J*(P–H) = 10 Hz, 9H). MS (EI) *m/e*: 514 [P⁺]. Anal. calcd. for C₂₂H₂₁Cr₂O₃P: C 51.37, H 3.72; found: C 51.27, H 3.71.

Preparation of [C₆H₅Cr(CO)₃]₂PEt, 9

The same procedure used for the synthesis of **8** was followed for the preparation of **9** from EtPCl₂, as a yellow crystalline solid (65% yield). IR (KBr) ν (CO): 1962 (s), 1851 (s, br) cm⁻¹. ³¹P{¹H} NMR (121.42 MHz, CDCl₃) δ : -5.5 (s). ¹H NMR (300 MHz, CDCl₃) δ : 5.4 (t, *J*(H–H) = 6 Hz, 6H), 5.2 (t, *J*(H–H) = 6 Hz, 4H), 1.8 (q, *J*(H–H) = 6 Hz, 4H), 1.2 (m, 6H). MS (EI) *m/e*: 486 [P⁺]. Anal. calcd. for C₂₀H₁₅O₆Cr₂P: C 49.39, H 3.12; found: C 49.75 H 3.34.

Preparation of $[C_6H_5Cr(CO)_3]$ PPh, 7

The same procedure was followed for the preparation of **7** from PhPCl₂ as a yellow crystalline solid (70% yield). IR (Nujol) ν CO): 1970 (s), 1900 (s, br), cm⁻¹. ³¹P{¹H} NMR (121.42 MHz, CDCl₃) δ : -4.0 (s). ¹H NMR (300 MHz, CDCl₃) δ : 7.3–7.6 (m, 5H), 5.6 (t, *J*(H–H) = 6 Hz, 4H), 5.3 (t, *J*(H–H) = 6 Hz, 2H), 5.2 (d, *J*(H–H) = 6 Hz, 4H). MS (EI) *m/e*: 534 [P⁺]. Anal. calcd. for C₂₄H₁₅CrO₆P: C 53.94, H 2.83; found: C, 53.60, H 2.85.

Preparation of $[C_6H_5(CO)_3]$ AsPh₂, 10

The same procedure was followed for the preparation of **10** from PhAsI₂ as a yellow solid (70% yield). MS (EI) *m/e*: 578 [P⁺]. ¹H NMR (300 MHz, CDCl₃) δ : 7.4 (br s, 5H), 5.5 (t, 4H), 5.3 (t, 2H), 5.15 (s, 4H). Anal. calcd. for C₂₄H₁₅CrO₆As: C 49.84, H 2.62; found: C 49.50, H 2.43.

Procedure A. Preparation of

$Ru_3(CO)_{11}$][AsMe₂(C₆H₅Cr(CO)₃)], 11

A freshly prepared Na(Ph₂CO) solution was added dropwise to a rapidly stirred solution of Ru₃(CO)₁₂ (200 mg, 0.31 mmol) and (CH₃)₂As[C₆H₅Cr(CO)₃] (100 mg, 0.31 mmol) in THF (25 mL) until the solution darkened in color (typically 5-10 drops). When TLC examination of the reaction mixture showed that no starting material remained, the solvent was removed in vacuo. The resulting dark red oil was dissolved in CH_2Cl_2 (3 mL) and was chromatographed on a silica gel column with CH_2Cl_2 -hexanes (1:1.4) as eluent to give three bands. Band 1 (yellow) was Ru₃(CO)₁₂ (trace amount) identified by IR spectroscopy and TLC. Band 3 was the disubstituted ruthenium cluster $Ru_3(CO)_{10}[AsMe_2(C_6H_5Cr(CO)_3)]_2$ 8 (trace amount). Band 2 gave red crystalline 11 (245 mg, 85%) yield). IR (KBr) ν (CO): 2100 (m), 2040 (s), 2020 (s), 1890 (sh), 1900 (s) cm⁻¹. ¹H NMR (300 MHz, CDCl₂) δ: 1.9 (s, 6H), 5.3 (t, J(H-H) = 6.6 Hz, 2H), 5.4 (d, J(H-H) = 6 Hz, 2H), 5.6 (t, J(H-H) = 6.6 Hz, 1H). Mass spectrum (FAB): *m/e*: 931 [P⁺]. Anal. calcd. for C₂₂H₁₁AsCrO₁₄Ru₃: C 28.43, H 1.20; found: C 28.14, H 1.23.

Procedure B. Preparation of

$Ru_3(CO)_{10}[AsMe_2(C_6H_5Cr-(CO)_3)]_2, 12$

The title compound was prepared in a way similar to that used for the monosubstituted compound **11** except that a little over 2 equivalents of the arsine (210 mg, 0.62 mmol) was used. The product was purified by using column chromatography with CH_2Cl_2 -hexanes (1:1) as eluent and was isolated in 70% yield. ¹H NMR (300 MHz, CDCl₃) δ : 5.5 (t, J(H-H) = 6 Hz, 2H), 5.4 (d, J(H-H) = 6.3 Hz, 4H), 5.2 (m, 4H), 1.8 (s, 12H). Mass spectrum (FAB): *m/e*: 1223 [P⁺]. Anal. calcd. for $C_{32}H_{22}As_2Cr_2ORu_3$: C 31.51, H 1.82; found: C 31.29, H 1.93.

Procedure C. Preparation of

$Os_3(CO)_{11}[AsMe_2(C_6H_5Cr(CO)_3)], 13$

The compound $[Os_3(CO)_{11}(MeCN)]$ (200 mg, 0.22 mmol) was stirred in CH₂Cl₂ (30 mL) with Me₂AsC₆H₅Cr(CO)₃ (70 mg, 0.22 mmol) for 2 h at room temperature to afford a clear yellow solution. Silica gel (200–400 mesh, 5 mL) was then added to the crude solution and the solvent was removed *in vacuo*. The dried residual silica gel was added to the top of a silica gel column. By using CH₂Cl₂–hexanes (1:1:8) as eluent, the pure yellow **13** was obtained in 90% yield (235 mg) from the first band. ¹H NMR (300 MHz, CDCl₃) δ : 5.5 (t, 1H), 5.4 (d, 2H), 5.2 (t, 2H), 2.0 (s, 6H). Mass spectrum (FAB) *m/e*: 1198 [P⁺]. Anal. calcd. for C₂₂H₁₁AsCrO₁₄Os₃: C 22.08, H 0.93; found: C 22.16, H 0.98. The second band that was eluted gave a small amount of the disubstituted cluster derivative identified by using mass spectrometry.

Procedure D. Preparation of Os₃(CO)₁₀[AsMe₂C₆H₅Cr(CO)₃]₂, 14

The procedure used for the preparation of 14 was identical to that used for 13 with the exception that $[Os_3(CO)_{10}(MeCN)_2]$ (100 mg, 0.1 mmol) was used. Pure 14 was thus obtained in 70% yield. ¹H NMR (300 MHz, CDCl₃) δ : 5.5 (t, 4H), 5.2 (t, 6H), 1.9 (s, 12H).Mass spectrum (FAB) *m/e*: 1487 [P⁺]. Anal. calcd. for $C_{32}H_{22}As_2Cr_2O_{16}Os_3$: C 25.85, H 1.49; found: C 25.71, H 1.57.

Procedure E. Preparation of Ru₃(CO)₁₁[PPr¹2C₆H₅Cr(CO)₃], 15

Addition of PPN⁺Cl⁻ (10 mg) to a solution of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and $Pr_{2}^{i}PC_{6}H_{5}(CO)_{3}$ (103 mg, 0.31 mmol) in THF (40 mL) resulted in gas evolution. After stirring for 30 min, the solvent was removed from the red solution under reduced pressure. The residue was dissolved in CH_2Cl_2 (2 mL) and applied to a silica gel column, with CH_2Cl_2 hexanes (1:1.7) as eluent. The first band proved to contain Ru₃(CO)₁₂ and the third band was characterized as $Ru_3(CO)_{10}[PPr_2^iC_6H_5(CO)_3]_2$. The major second band afforded 15 as a red powder in 80% yield after solvent evaporation. Crystals of 15 were grown from CH₂Cl₂-hexanes (1:2.5) at -30° C. The crystals thus obtained were washed with hexanes and dried in vacuo for 1 min. IR (CH₂Cl₂) ν (CO): 2100 (s), 2049 (vs), 2017 (vs), 1978 (vs), 1907 (vs) cm⁻¹. 942 $[P^+]$. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ : 58.9 (s). ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3) \delta: 5.7 (t, J(H-H) = 6.2 \text{ Hz}, 3H), 5.2 (t, J(H-H))$ H) = 6.3 Hz, 2H), 2.5 (m, 2H), 1.2-1.4 (m, 12H). Mass spectrum (FAB) m/e: Anal. calcd. for C₂₆H₁₉CrO₁₄PRu₃: C 33.16, H 2.03; found: C 32.84, H 1.90.

Procedure F. Preparation of

$Ru_{3}(CO)_{10}[Pr_{2}^{1}PC_{6}H_{5}Cr(CO)_{3}]_{2}, 16$

The title complex was prepared in the same manner as described for the preparation of the monosubstituted cluster **15** except that a little over 2 molar equivalents of $Pr_{2}PC_{6}H_{5}Cr(CO)_{3}$ (215 mg, 0.65 mmol) was used. Following chromatography with $CH_{2}Cl_{2}$ -hexanes (1:1.3) as eluent, pure **16** was obtained in 70% yield as a dark red powder. X-ray-quality crystals were grown from $CH_{2}Cl_{2}$ -hexanes (1:2.5) at $-4^{\circ}C$. IR (KBr) ν (CO): 2022 (s), 1973 (vs), 1903 (vs) cm⁻¹. ³¹P{¹H} NMR (121.4 MHz, CDCl_{3}) δ : 54.6 (s). ¹H NMR (300 MHz, CDCl_{3}) δ : 5.75 (t, 6H), 5.2 (t, J(H–H) = 6.3 Hz, 4H), 2.5 (m, J(H–H)=6.1 Hz, 4H), 1.2–1.4 (m, 24H). Mass spectrum (FAB) *m/e*: 1244 [P⁺]. Anal. calcd. for C₄₁H₄₀Cl₂Cr₂O₁₆P₂Ru₃: C 37.06, H 3.04. found: C 37.03, H 2.97.

Preparation of $Os_3(CO)_{11}[Pr_2^iPC_6H_5Cr(CO)_3]$, 17

The yellow complex **17** was obtained in 80% yield by using procedure C. IR (KBr) ν (CO): 2100 (w), 2050 (s), 2030-2000 (vs, br), 1990-1960 (vs, br), 1940 (w), 1910 (s), 1890 (s) cm⁻¹. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ : 27.8 (s). ¹H NMR (300 MHz, CDCl₃) δ : 5.7 (t, 3H), 5.2 (t, 2H), 2.5 (m, 2H), 1.2-1.4 (m, 12H). Mass spectrum (FAB) *m/e*: 1209 [P⁺]. Anal. calcd. for C₂₆H₁₉CrO₁₄Os₃P: C 25.83, H 1.59; found: C 25.89, H 1.59.

Preparation of Os₃(CO)₁₀[Pr¹₂PC₆H₅Cr(CO₃]₂, 18

The yellow complex **18** was isolated in 80% yield by using procedure **D**. IR (KBr) ν (CO): 2080 (m), 2010 (sh), 2000 (vs), 1970 (vs), 1900 (s, br) cm⁻¹. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ : 21.7 (s). ¹H NMR (300 MHz, CDCl₃) δ : 5.7 (t, 6H), 5.2 (t, 4H), 2.4 (m, 4H), 1.1–1.4 (m, 24H). Mass spectrum (FAB) *m/e*: 1513 [P⁺]. Anal. calcd. for C₄₀H₃₈Cr₂O₁₆Os₃P₂: C 31.79, H 2.54; found: C 31.63, H 2.50.

Preparation of Ru₃(CO)₁₁[Ph₂PC₆H₅Cr(CO)₃], 19

The complex **19** was isolated, by following procedure **A**, as a red powder (~70% yield). This powder was dissolved in CH₂Cl₂ (10 mL), layered with hexanes (20 mL), and stored in a freezer for a week to give red-orange prism-like crystals. IR (Nujol) ν (CO): 2100 (s), 2060 (sh), 2040 (s), 2020 (vs), 2000 (vs), 1970 (vs), 1960 (sh), 1900 (s) cm⁻¹. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ : 37.3 (s). ¹H NMR (300 MHz, CDCl₃) δ : 7.4–7.6 (br s, 10H), 5.6 (t, *J*(H–H) = 6 Hz, 3H), 5.1 (t, *J*(H–H) = 6 Hz, 2H). Mass spectrum (FAB) *m/e*: 1011 [P⁺]. Anal. calcd. for C₃₂H₁₅CrO₁₄PRu₃: C 38.07, H 1.50; found: C 38.21, H 1.55.

$Ru_{3}(CO)_{10}[Ph_{2}PC_{6}H_{5}Cr(CO)_{3}]_{2}, 20$

Compound **20** was isolated in 60% yield by following procedure **B**. ${}^{31}P{}^{1}H{}$ NMR (121.4 MHz, CDCl₃) δ : 36.5 (s). ${}^{1}H{}$ NMR (300 MHz, CDCl₃) δ : 7.4–7.6 (br s, 5H), 5.5 (t, 6H), 5.1 (t, 4H). Mass spectrum (FAB) *m/e*: 1381 [P⁺]. Anal. calcd. for C₅₂H₃₀Cr₂O₁₆P₂Ru₃: C 45.26, H 2.20; found: C 45.39, H 2.28.

Preparation of Os₃(CO)₁₁[Ph₂PC₆H₅Cr(CO)₃], 21

Solid **21** was obtained in 80% yield by following procedure **C**. IR (KBr): ν (CO) 2150 (s), 2060 (vs), 2020 (vs), 2000 (vs), 1970 (vs), 1900 (vs) cm⁻¹. ³¹P{¹H} NMR (121.4 MHz, CD₂Cl₂) δ : 0.3 (s). ¹H NMR (300 MHz, CD₂Cl₂) δ : 7.5 (m, 10H), 5.8 (td, *J*(H–H) = 5.8 Hz, 1H), 5.6 (td, *J*(H–H) = 5.7 Hz, 2H), 5.2 (td, J(H-H) = 5.8 Hz, 2H). Mass spectrum (FAB) *m/e*: 1277 [P⁺]. Anal. calcd. for C₃₂H₁₅CrO₁₄Os₃P: C 30.07, H 1.19; found: C 30.15, H 1.23.

Preparation of Ru₃(CO)₁₁[Et₂PC₆H₅Cr(CO)₃], 22

Compound 22 was obtained in 85% yield by using procedure A. ${}^{31}P{}^{1}H{}$ NMR (121.4 MHz, CDCl₃) δ : 28.2 (s). IR (KBr): 2100 (s), 2040 (s), 2020 (s), 1980 (vs), 1970 (vs), 1950 (s), 1900 (s), 1870 (s) cm⁻¹. ${}^{1}H{}$ NMR (300 MHz, CDCl₃) δ : 5.5 (td, *J*(H–H) = 7 Hz, 1H), 5.3 (td, *J*(H–H) = 7 Hz, 2H), 5.2 (2dd, *J*(H–H) = 7 Hz, 2H), 2.0–2.4 (m, 4H), 1.2–1.4 (2t, *J*(H–H) = 7 Hz, 6H). Mass spectrum (FAB) *m/e*: 915 [P⁺]. Anal. calcd. for C₂₄H₁₅CrO₁₄PRu₃: C 31.55, H 1.66; found: C 31.47, H 1.66.

Preparation of Ru₃(CO)₁₀[Et₂PC₆H₅Cr(CO)₃]₂, 23

The dark red product **23** was isolated in 75% yield by using procedure **B**. IR (KBr) ν (CO): 2070 (w), 2020 (s), 2000–1910 (s, br), 1910–1880 (s, br), cm⁻¹. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ : 28.4 (s). ¹H NMR (300 MHz, CDCl₃) δ : 5.6 (t, *J*(H–H) = 7 Hz, 1H), 5.4 (t, *J*(H–H) = 7 Hz, 2H), 5.2 (d, *J*(H–H) = 7 Hz, 2H), 2.0–2.4 (m, 8H), 1.2–1.5 (2t, *J*(H–H) = 7 Hz, 12H). Mass spectrum (FAB) *m/e*: 1189 [P⁺]. Anal. calcd. for C₃₈H₃₂Cl₂Cr₂O₁₆P₂Ru₃: C 34.91, H 2.54; found: C 34.74, H 2.59.

Preparation of Os₃(CO)₁₁[Et₂PC₆H₅Cr(CO)₃], 24

The yellow product **24** was obtained in 80% yield by following procedure E.IR (KBr) ν (CO): 2100 (m), 2060 (s), 2030 (s), 2000 (vs), 1980 (sh), 1970 (vs), 1910 (s), 1900 (sh), 1880 (s), 1870 (sh), cm⁻¹. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ : -9.1 (s). ¹H NMR (300 MHz, CDCl₃) δ : 5.5 (t, *J*(H–H) = 7 Hz, 1H), 5.4 (t, *J*(H–H) = 7 Hz, 2H), 5.2 (d, *J*(H–H) = 7 Hz, 2H), 2.2–2.4 (m, 4H), 1.2–1.4 (t, *J*(H–H) = 7 Hz, 6H). Mass spectrum (FAB) *m/e*: 1182 [P⁺]. Anal. calcd. for C₂₄H₁₅CrO₁₄Os₃P: C 24.40, H, 1.28; found: C 24.56, H 1.31.

Preparation of Os₃(CO)₁₀[Et₂PC₆H₅Cr(CO)₃]₂, 25

The use of procedure **D** afforded **25** in 70% yield. IR (KBr) ν (CO): 2075 (m), 2010 (sh), 1980 (vs, br), 1890 (s, br) cm⁻¹. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ : -9.8 (s). ¹H NMR (300 MHz, CDCl₃) δ : 5.5 (t, *J*(H–H) = 7 Hz, 1H), 5.3 (t, *J*(H–H) = 7 Hz, 2H), 5.2 (d, *J*(H–H) = 7 Hz, 2H), 2.2–2.6 (m, 4H), 1.2–1.5 (2t, *J*(H–H) = 7 Hz, 6H). Mass spectrum (FAB) *m/e*: 1456 [P⁺]. Anal. calcd. for C₃₆H₃₀Cr₂O₁₆Os₃P₂: C 29.71, H 2.08. found: C 29.96, H 2.14.

Preparation of Os₃(CO)₉[Et₂PC₆H₅Cr(CO)₃]₃, 26

A solution of $Os_3(CO)_{11}[Et_2PC_6H_5Cr(CO)_3]$ (300 mg) was heated in refluxing n-octane under a nitrogen atmosphere for 15 h. After this time TLC showed that no starting material was present. The solvent was then removed under reduced pressure and the resulting brown oil was transferred to a silica gel column. Elution with hexane gave one yellow band, which was $Os_3(CO)_{12}$, as identified by IR spectroscopy. Subsequent elution with hexanes- CH_2Cl_2 (1:1.7) afforded three bands. Bands 1 and 3 contained trace amounts of unidentified products. The major band 2 contained the complex **26**. Orange crystals suitable for X-ray structure analysis were grown from hexanes- CH_2Cl_2 (3:1) at -30° C. IR (KBr) ν (CO): 1965 (vs, br), 1930 (s), 1890 (vs, Br) cm⁻¹. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ : -15.9 (s). ¹H NMR (300 MHz, CDCl₃) δ : 5.6 (t, *J*(H–H) = 7 Hz, 3H), 5.4 (t, *J*(H–H) = 7 Hz, 6H), 5.2 (d, *J*(H–H) = 7 Hz, 6H), 2.0–2.5 (m, 12H), 1.2–1.4 (m, 18H). Mass spectrum (FAB) *m/e*: 1729 [P⁺]. Anal. calcd. for C₄₈H₄₅Cr₃Os₃P₃: C 33.33, H 2.63; found: C 32.93, H 2.62.

Preparation of Ru₃(CO)₁₁[PhP{C₆H₅Cr(CO)₃}₂], 27

The title compound was prepared by three different methods but always in low yield. Method A resulted in 25% yield and method E in 15% yield. An excess of PhP[C₆H₅Cr(CO)₃]₂ (200 mg) was added to a cool solution of Ru₃(CO)₁₁(MeCN) (100 mg, 0.15 mmol, 20 mL of CH₂Cl₂) generated in situ. The resulting solution was stirred for 1 h and the solvent was removed *in vacuo*. The ³¹P NMR spectrum of the crude product indicated the presence of **27** in low yield.

27: yellow solid. IR (CH₂Cl₂) ν (CO): 2100 (s), 2050 (s), 2040 (s), 1970 (s), 1900 (s) cm⁻¹. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ : 37.6 (s). ¹H NMR (300 MHz, CDCl₃) δ : 7.4–7.6 (m, 5H), 5.8 (m, 6H), 5.3 (m, 4H). Mass spectrum (FAB) *m/e*: 1147 [P⁺]. Anal. calcd. for C₃₅H₁₅Cr₂O₁₇PRu₃: C 36.69, H 1.32; found: C 36.65, H 1.40.

Preparation of Os₃(CO)₁₁[PhP{C₆H₅Cr(CO)₃}₂], 28

The yellow solid **28** was isolated in 50% yield by using procedure C. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ : 0.1 (s). ¹H NMR (300 MHz, CDCl₃) δ : 7.6 (m, 2H), 7.4 (m, 3H), 5. 7 (t, 6H), 5.4 (q, 4H). Mass spectrum (FAB) *m/e*: 1415 [P⁺]. Anal. calcd. for C₃₅H₁₅Cr₂O₁₇Os₃P: C 29.75, H, 1.07; found: C 29.50, H 1.31.

Preparation of Ru₃(CO)₁₁[Ph₂AsC₆H₅Cr(CO)₃], 29

The red product **29** was obtained in 10% yield by following procedure **A**. ³¹P{¹H} NMR (121.4 MHz, CDCl₃) δ : 7.3 (m, 10H), 5.3 (t, 2H), 5.1 (3H). Mass spectrum (FAB) *m/e*: 1054 [P⁺]. Anal. calcd. for C₃₂H₁₅AsCrO₁₄Ru₃: C 36.48, H 1.44; found: C 36.64, H 1.56.

X-ray crystallographic analyses

Crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with $2\theta = 27.8-33.1^{\circ}$ for 3, 35.7-40.1° for 15, 20.1-30.7° for 19, 30.1°-36.8° for 16, and 40.1°-45.5° for 26. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, decayed linearly by 7.8% for 15 and by 2.1% for 19 and showed only small random fluctuations for other complexes. The data were processed and corrected for Lorentz and polarization effects, decay (where appropriate), and absorption (empirical, based on azimuthal scans for three reflections).²

The structures were solved by the Patterson method. The structural analysis of **26** was initiated in the centrosymmetric space group $P\overline{3}$ on the basis of the *E*-statistics and the Patterson function. This choice was confirmed by subsequent calculations. Complex **16** has exact (crystallographic) C_2 symmetry and complex **26** has exact C_3 symmetry.

The dichloromethane solvent in 16 was modeled as 1:1 disordered over two sites, both carbon atoms lying on the twofold

² teXsan: Crystal structure analysis package. Molecular Sturcture Corp., The Woodlands, Tex. 1985 and 1992.

Compound	3	15	19	16	26
Formula	C ₁ ,H ₁₀ CrO ₂ P	$C_{2}H_{10}CrO_{14}PRu_{2}$	$C_{13}H_{14}CrO_{14}PRu_{2}$	$C_{40}H_{20}Cr_{2}O_{12}P_{2}Ru_{2}CH_{2}Cl_{2}$	C ₄₀ H ₄ Cr ₂ O ₁₂ Os ₂ P ₂
Fw	330.28	941.61	1009.64	1328.81	1729.38
Color, habit	Yellow, prism	Golden, prism	Red-orange, prism	Black, prism	Red-brown, prism
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Trigonal
Space group	$P2_1/c$	$P2_1/n$	Pbca	P2,2,2	P3
a, Å	8.150(2)	8.565(2)	17.367(4)	13.832(3)	15.7758(4)
<i>b</i> , Å	13.490(2)	21.808(3)	24.471(5)	17.558(2)	15.7758(4)
<i>c</i> , Å	15.125(1)	17.167(3)	16.096(3)	10.144(1)	12.662(1)
α, deg	90	90	90	90	90
β, deg	100.19(1)	97.41(2)	90	90	90
γ, deg	90	90	90	90	120
V, Å ³	1636.8(4)	3179.5(10)	6840(2)	2463.7(7)	2722.2(3)
Ζ	4	4	8	2	2
$\rho_{calc}, g/cm^3$	1.340	1.967	1.960	1.791	2.110
F(000)	688	1832	3920	1316	1644
μ (Mo- K_{α}), cm ⁻¹	8.00	18.10	16.89	15.65	77.00
Crystal size, mm	$0.40 \times 0.40 \times 0.50$	$0.18 \times 0.30 \times 0.40$	$0.25 \times 0.35 \times 0.45$	$0.16 \times 0.25 \times 0.39$	$0.20 \times 0.25 \times 0.40$
Transmission factors	0.84-1.00	0.84-1.00	0.89-1.00	0.88-1.00	0.54-1.00
Scan type	ω–2θ	ω–2θ	ω	ω–2θ	ω–2θ
Scan range, ω°	$1.10 + 0.35 \tan \theta$	$1.30 + 0.35 \tan \theta$	$0.94 + 0.35 \tan \theta$	$1.26 + 0.35 \tan \theta$	$1.42 + 0.35 \tan \theta$
Scan, ° min ⁻¹	32	16	16	16	32
Data collected	+ <i>h</i> , + <i>k</i> , $\pm l$	$+h, +k, \pm l$	+h, +k, +l	+h, +k, +l	$\pm h$, +k, +l
$2\theta_{max}$, deg	55	55	55	60	70
Crystal, decay, %	7.8	2.1	Negligible	Negligible	
Total reflections	4195	7987	8579	4035	8652
Unique reflections	3929	7492	8579	4035	8006
R _{merge}	0.020	0.029	_	_	0.044
Number with $I \ge 3\sigma(I)$	2326	4410	3878	3046	4093
Variables	182	406	460	307	227
R	0.031	0.027	0.029	0.025	0.029
R_{w}	0.027	0.024	0.024	0.023	0.025
gof	2.25	1.67	1.41	1.68	1.35
Max Δ/σ (final cycle)	0.001	0.001	0.003	0.01	0.001
Residual density e/Å ³	-0.21 to 0.23	-0.38 to 0.38	-0.44 to 0.42	-0.45 to 0.41	-1.36 to 1.28 (near Os)

Table 1. Crystallographic data.^a

^aTemperature 294 K, Rigaku AFC6S diffractometr, MoK_a ($\lambda = 0.71069$ Å) radiation, graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), $\sigma U2.(F^2) = [S^2(C + 4B)]/Lp^2$ (S = scan rate, C = scan count, B = normalized background count), function minimized $\Sigma w(|F_0| - |F_c|)^2$ where $w = 4F_0^2/\sigma^2(F_0^2)$, $R = \Sigma ||F_0| - |F_c|/\Sigma ||F_0|$, $R_w = (\Sigma w(|F_0| - |F_c|)^2/\Sigma w |F_0|^2)^{1/2}$, and gof = $[\Sigma w(|F_0| - |F_c|)^2/(m - n)]^{1/2}$. Values given for R, R_w , and gof are based on those reflections with $I \ge 3\sigma(I)$.

axis. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in calculated positions (C—H = 0.98 Å, $B_{\rm H} = 1.2 B_{\rm bonded atom}$). Secondary extinction corrections were applied for **3** and **26**, the final values of the extinction coefficients being $1.13(3) \times 10^{-6}$ and $3.9(2) \times 10^{-7}$, respectively. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the *International Tables for X-Ray Crystallography* (13). A parallel refinement of the mirror image of **16** gave significantly higher residuals, the *R* and R_w ratios being 1.083 and 1.100, respectively. Final atomic coordinates and equivalent isotropic thermal parameters, selected bond lengths, and selected bond angles appear in Tables 2–4, respectively. Hydrogen atom parameters, anisotropic thermal parameters, bond lengths, bond angles, torsion

angles, intermolecular contacts, and least-squares planes are included as supplementary material. $^{\rm 3}$

Results and Discussion

Two different strategies were utilized previously to prepare

³ Copies of material on deposit may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0S2. Tables of hydrogen atom coordinates and bond lengths and angles involving hydrogen atoms have also been deposited with the Cambridge Crystallograhic Data Centre and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ, UK.

Table 2. Final atomic coordinates and B_{eq} (Å²).^{*a*}

	Atom	x	у	z	B _{eq}	Atom	x	у	z	B _{eq}
	3					C(18)	-0.0232(6)	0.1786(2)	0.5720(3)	4.8(1)
	Cr(1)	0.47528(5)	0.16413(3)	0.12765(3)	3,656(9)	C(19)	0.0984(6)	0.2224(2)	0.5774(3)	4.9(1)
	P(1)	0.76735(9)	0.36299(5)	0.22499(5)	4 19(2)	C(20)	0.1891(6)	0.2290(2)	0.5164(3)	4.0(1)
	0(1)	0.1355(3)	0.0742(2)	0.1022(2)	8.49(8)	C(21)	0.4053(5)	0.2631(2)	0.3845(3)	4.0(1)
	O(2)	0.4576(3)	0.1604(2)	-0.0705(1)	720(7)	C(22)	0.0755(5)	0.2755(2)	0.3206(3)	3.8(1)
	O(3)	0.3048(3)	0.3606(2)	0.1004(2)	8 29(8)	C(23)	0.5425(5)	0.2239(2)	0.4187(3)	4.5(1)
	C(1)	0.2675(4)	0.1075(2)	0.1126(2)	5.22(0)	C(24)	0.4469(6)	0.3033(2)	0.3169(3)	5.1(1)
14	C(2)	0.4637(3)	0.1607(2)	0.0065(2)	4 56(7)	C(25)	0.0626(7)	0.3285(2)	0.3785(3)	4.9(1)
12/	C(3)	0.3710(4)	0.2850(2)	0.0005(2) 0.1128(2)	5 25(8)	10				(1)
11/	C(4)	0.7011(3)	0.2328(2)	0.2097(2)	3 68(6)	$\mathbf{I}\mathbf{J}$	0 10222(2)	0.05218(2)	0.07277(2)	2 5 42(0)
n]	C(5)	0.7506(3)	0.1647(2)	0.1493(2)	3.98(6)	$\operatorname{Ru}(1)$	0.19333(2)	0.03216(2)	0.07377(3)	2.543(9)
γo	C(6)	0.6944(3)	0.0654(2)	0.1457(2)	4 63(7)	$\operatorname{Ru}(2)$	0.29699,3)	-0.03793(2)	0.07451(3)	3.048(10)
E	C(7)	0.5893(4)	0.0001(2)	0.2030(2)	5.03(7)	$C_r(1)$	0.32003(2)	0.03400(2)	-0.03040(3)	2.637(9)
SS	C(8(0.5387(4)	0.0998(2)	0.2638(2)	4 90(8)	$\mathbf{U}(1)$	0.05471(5)	0.19110(4)	0.23157(5)	3.50(2)
Ē	C(9)	0.5927(3)	0.0990(2) 0.1977(2)	0.2050(2)	4.90(0)	P(1)	0.13848(7)	0.13703(6)	0.03412(9)	2.46(3)
	C(10)	0.3527(3)	0.1977(2) 0.3950(2)	0.2000(2) 0.1231(2)	4.40(7)	O(1)	0.0924(3)	0.0013(2)	0.2055(3)	6.1(1)
5	C(11)	0.0522(5) 0.7138(4)	0.3730(2) 0.4044(2)	0.1231(2)	4.75(7)	O(2)	0.0880(2)	-0.0016(2)	-0.0563(3)	5.4(1)
z	C(12)	0.7150(4)	0.4030(2)	0.0713(2) 0.1308(2)	0.20(9)	O(3)	0.2784(2)	0.1028(2)	0.2212(2)	4.2(1)
00	C(12)	0.9400(4)	0.4757(2)	0.1338(2) 0.3116(2)	5 54(8)	O(4)	0.4324(3)	-0.1146(2)	0.0361(3)	7.2(2)
ž	C(13)	0.9301(4)	0.3441(2) 0.3100(3)	0.3110(2)	3.34(8)	0(5)	0.2184(2)	-0.1068(2)	0.2047(3)	5.9(1)
Щ	C(14)	1.0802(4)	0.3100(3)	0.4000(2)	0.4(1)	O(6)	0.2050(3)	-0.0903(2)	-0.0658(3)	5.7(1)
Ū	C(15)	1.0892(4)	0.2708(3)	0.2851(2)	7.4(1)	0(7)	0.3977(2)	0.0135(2)	0.2131(2)	4.4(1)
y.	15					O(8)	0.4722(2)	-0.0026(2)	-0.0969(3)	5.8(1)
u la	Ru(1)	0.26285(4)	0.14078(2)	0.25719(2)	2.724(7)	O(9)	0.4191(2)	0.1142(2)	0.1060(2)	5.0(1)
0.0 0.0	Ru(2)	0.00277(4)	0.05429(2)	0.21906(2)	2.878(7)	O(10)	0.3431(3)	0.1596(2)	-0.1275(3)	5.4(1)
su	Ru(3)	0.27305(4)	0.04980(2)	0.13654(2)	3.212(8)	0(11)	0.2320(2)	0.0078(2)	-0.1725(3)	5.1(1)
nal	Cr(1)	0.19885(9)	0.13304(3)	0.55400(4)	3.64(2)	O(12)	0.1279(3)	0.1023(2)	0.3315(3)	6.8(2)
so	P(1)	0.2265(1)	0.21630(5)	0.35364(6)	2.98(2)	O(13)	0.1997(3)	0.2559(2)	0.2468(3)	7.4(2)
pei	O(1)	0.5887(4)	0.1710(2)	0.2216(2)	5.27(10)	O(14)	0.0055(3)	0.2341(2)	0.3975(3)	6.5(1)
or	O(2)	0.4018(4)	0.0553(2)	0.3903(2)	4.89(9)	C(1)	0.1277(3)	0.0212(2)	0.1550(4)	3.6(2)
F	O(3)	0.1380(4)	0.2368(2)	0.1352(2)	5.8(1)	C(2)	0.1317(3)	0.0179(2)	-0.0118(4)	3.5(1)
Г. М	O(4)	0.1494(4)	-0.0580(2)	0.0350(2)	5.9(1)	C(3)	0.2514(3)	0.0836(2)	0.1638(3)	3.0(1)
M N	O(5)	0.5758(5)	0.0710(2)	0.0657(3)	9.4(2)	C(4)	0.3837(4)	-0.0855(3)	0.0487(4)	4.4(2)
n v	O(6)	0.4497(5)	-0.0354(2)	0.2599(2)	8.2(1)	C(5)	0.2482(3)	-0.0808(3)	0.1556(4)	3.9(2)
roi	O(7)	0.1279(5)	0.1411(2)	0.0116(2)	5.9(1)	C(6)	0.2384(4)	-0.0688(2)	-0.0163(4)	4.1(2)
df	O(8)	-0.1799(5)	-0.0426(2)	0.1158(2)	6.0(1)	C(7)	0.3605(3)	-0.0020(2)	0.1610(4)	3.3(1)
qe	O(9)	-0.2494(4)	0.0740(2)	0.3250(2)	6.0(1)	C(8)	0.4191(3)	0.0181(2)	-0.0724(4)	3.7(1)
loa	O(10)	0.1477(5)	-0.0424(2)	0.3362(2)	7.2(1)	C(9)	0.3826(3)	0.0900(2)	0.0601(3)	2.2(1)
ММ	O(11)	-0.1429(4)	0.1556(2)	0.1103(2)	5.34(10)	C(10)	0.3352(3)	0.1209(2)	-0.0900(3)	3.3(1)
Ô	O(12)	0.5510(5)	0.1270(2)	0.5793(3)	9.0(2)	C(11)	0.2644(3)	0.0233(2)	-0.1164(4)	3.4(1)
J. I	O(13)	0.2065(6)	-0.0008(2)	0.5185(3)	8.3(1)	C(12)	0.1000(4)	0.1358(3)	0.2919(4)	4.5(2)
len	O(14)	0.2194(5)	0.0989(2)	0.7237(2)	7.0(1)	C(13)	0.1453(4)	0.2307(3)	0.2410(4)	4.8(2)
Ū	C(1)	0.4659(5)	0.1601(2)	0.2374(2)	3.6(1)	C(14)	0.0241(3)	0.2180(3)	0.3329(4)	4.3(2)
J.	C(2)	0.3427(5)	0.0844(2)	0.3402(2)	3.2(1)	C(15)	0.0626(3)	0.1649(2)	0.1004(3)	2.8(1)
an.	C(3)	0.1776(5)	0.1986(2)	0.1788(3)	3.7(1)	C(16)	0.0466(3)	0.2215(2)	0.1033(3)	3.7(1)
C	C(4)	0.1952(5)	-0.0183(2)	0.0737(3)	4.0(1)	C(17)	-0.0162(4)	0.2419(3)	0.1472(4)	4.8(2)
A sparada	C(5)	0.4663(6)	0.0637(3)	0.0946(3)	5.3(1)	C(18)	-0.0643(3)	0.2059(3)	0.1902(4)	5.1(2)
	C(6)	0.3803(5)	-0.0025(3)	0.2181(3)	5.3(1)	C(19)	-0.0517(3)	0.1497(3)	0.1883(4)	4.5(2)
	C(7)	0.1742(5)	0.1088(2)	0.0609(3)	4.1(1)	C(20)	0.0127(3)	0.1297(2)	0.1445(3)	3.4(1)
	C(8)	-0.1091(5)	-0.0075(2)	0.1541(3)	3.8(1)	C(21)	0.0857(3)	0.1330(2)	-0.0648(3)	2.7(1)
	C(9)	-0.1531(5)	0.0681(2)	0.2865(3)	3.9(1)	C(22)	0.0066(3)	0.1287(3)	-0.0653(4)	4.5(2)
:	C(10)	0.1033(5)	-0.0054(2)	0.2935(3)	4.4(1)	C(23)	-0.0313(4)	0.1230(3)	-0.1402(5)	6.1(2)
1	C(11)	-0.0790(5)	0.1198(2)	0.1510(3)	3.6(1)	C(24)	0.0071(4)	0.1211(3)	-0.2143(4)	5.1(2)
1	C(12)	0.4160(7)	0.1304(3)	0.5678(3)	5.4(1)	C(25)	0.0854(4)	0.1254(3)	-0.2133(4)	4.6(2)
	C(13)	0.2032(7)	0.0504(3)	0.5301(3)	5.1(1)	C(26)	0.1238(3)	0.1311(2)	-0.1389(4)	3.7(1)
	C(14)	0.2129(6)	0.1109(2)	0.6580(3)	4.8(1)	C(27)	0.2022(3)	0.1964(2)	0.0211(3)	2.5(1)
	C(15)	0.1565(5)	0.1945(2)	0,4463(2)	3.11(10)	C(28)	0.2630(3)	0.2044(2)	0.0749(4)	3.6(1)
	C(16)	0.0389(5)	0.1488(2)	0.4444(2)	3 5(1)	C(29)	0.3118(3)	0.2480(2)	0.0658(4)	4.8(2)
	C(17)	-0.0519(5)	0.1413(2)	0.5062(3)	4 3(1)	C(30)	0.3010(4)	0.2841(2)	0.0043(4)	4.8(2)

Table 2. (continued).

Atom	x	у	Z	Beq
C(31)	0.2414(4)	0.2782(3)	-0.0493(4)	5.2(2)
C(32)	0.1916(3)	0.2344(2)	-0.0407(4)	4.2(2)
16				
Ru(1)	0.58555(2)	0.54730(2)	0.38033(4)	2.289(6)
Ru(2)	0.50000	0.50000	0.62732(6)	2.777(10)
Cr(1)	0.66145(6)	0.74385(4)	0.06072(7)	3.04(2)
$Cl(1)^b$	0.9173(7)	0.4902(5)	0.7263(7)	17.7(3)
$Cl(1a)^b$	0.9088(7)	0.4983(4)	0.869(1)	20.4(4)
P(1)	0.71732(7)	0.63485(6)	0.3805(1)	2.21(2)
O(1)	0.6220(3)	0.4810(2)	0.1118(4)	6.0(1)
O(2)	0.7180(2)	0.4255(2)	0.4954(5)	5.4(1)
O(3)	0.4366(3)	0.6702(2)	0.3082(4)	4.91(10)
O(4)	0.6652(3)	0.5154(2)	0.8228(4)	6.0(1)
O(5)	0.4504(3)	0.6694(2)	0.6260(5)	5.19(10)
O(6)	0.5142(3)	0.6345(2)	-0.0431(5)	6.6(1)
O(7)	0.4999(3)	0.8191(2)	0.2073(4)	5.5(1)
O(8)	0.6058(4)	0.8496(3)	-0.1568(5)	9.2(2)
C (1)	0.6080(3)	0.5096(3)	0.2105(4)	3.5(1)
C(2)	0.6631(3)	0.4707(3)	0.4611(5)	3.4(1)
C(3)	0.4921(3)	0.6255(3)	0.3358(4)	3.13(10)
C(4)	0.6033(4)	0.5123(3)	0.7494(5)	3.6(1)
C(5)	0.4721(3)	0.6073(3)	0.6141(6)	3.8(1)
C(6)	0.5708(4)	0.6764(3)	-0.0035(6)	4.4(1)
C(7)	0.5632(3)	0.7894(3)	0.1536(5)	3.5(1)
C(8)	0.6281(5)	0.8085(4)	-0.0744(6)	5.5(2)
C(9)	0.7205(3)	0.7115(3)	0.5048(5)	2.82(10)
C(10)	0.0332(3)	0.7645(3)	0.4903(3)	3.3(1)
C(11)	0.7310(4)	0.0795(3)	0.0431(3)	3.9(1)
C(12)	0.8355(3)	0.5804(2)	0.4038(4)	2.90(9)
C(13)	0.9214(3)	0.0407(3)	0.4217(0)	4.3(1)
C(14)	0.8000(3)	0.5207(3)	0.2997(0)	238(0)
C(15)	0.7420(3)	0.6371(3)	0.2239(4) 0.1078(5)	3 03(9)
C(10)	0.7333(3)	0.0430(3)	-0.0072(5)	3.03(1)
C(18)	0.7899(4) 0.8122(4)	0.3772(4)	-0.0072(5)	4.5(1)
C(10)	0.0122(4) 0.7998(3)	0.8004(3)	0.0005(5)	3.8(1)
C(20)	0.7550(3)	0.7662(3)	0.2208(5)	3.08(10)
$C(21)^{b}$	1.0000	0.5000	0.835(3)	8.9(7)
$C(21a)^{b}$	1.0000	0.5000	0.950(2)	5.6(4)
26	10000	0.0000	01100(=)	
$\Delta 0$	0 54927(1)	0.24356(1)	0 18923(1)	2.046(6)
Cr(1)	0.34927(1) 0.27052(5)	0.37220(6)	0.18923(1) 0.28488(6)	2.040(0)
P(1)	0.39383(8)	0.37220(0) 0.21974(8)	0.20400(0)	2.24(3) 2 29(4)
O(1)	0.57505(0)	0.9372(2)	0.1023(3)	44(2)
O(2)	0.4334(3)	0.9972(2) 0.2010(3)	0.1025(3) 0.4216(3)	4.0(1)
O(2)	0.5756(3)	0.2010(3)	-0.0319(3)	4 3(2)
O(4)	0.0000(3) 0.1073(3)	0.3081(4)	0.1290(3)	6.0(2)
O(5)	0.1798(3)	0.4673(3)	0.4094(3)	5.3(2)
O(6)	0.1349(3)	0.1917(3)	0.4079(4)	6.4(2)
C(1)	0.3852(3)	0.3308(3)	0.2454(4)	2.6(2)
C(2)	0.3690(3)	0.3751(3)	0.1564(4)	3.1(2)
C(3)	0.3775(4)	0.4685(4)	0.1655(5)	4.0(2)
C(4)	0.4015(4)	0.5179(4)	0.2613(5)	4.3(2)
C(5)	0.4168(4)	0.4746(4)	0.3505(5)	4.0(2)
C(6)	0.4081(3)	0.3822(3)	0.3436(4)	3.1(2)
C(7)	0.3039(3)	0.1465(4)	0.1297(4)	3.4(2)
C(8)	0.1959(4)	0.1130(4)	0.1482(5)	5.1(3)

Can. J. Chem. Vol. 74, 1996

Table 2. (concluded).

Atom	x	у	z	B _{eq}
C(9)	0.3418(3)	0.1531(3)	0.3537(4)	3.2(2)
C(10)	0.3264(4)	0.0499(4)	0.3552(4)	4.1(2)
C(11)	0.4924(3)	0.1135(3)	0.1405(4)	2.8(2)
C(12)	0.5705(3)	0.2190(3)	0.3354(4)	3.0(2)
C(13)	0.5455(3)	0.2940(3)	0.0525(4)	2.9(2)
C(14)	0.1713(4)	0.3340(4)	0.1879(4)	4.0(2)
C(15)	0.2152(4)	0.4315(4)	0.3609(4)	3.4(2)
C(16)	0.1888(4)	0.2599(4)	0.3608(5)	4.1(2)

 ${}^{a}B_{eq} = (8/3)\pi^{2}\Sigma\Sigma U_{ij}a^{*}_{i}a^{*}_{j}(\mathbf{a}_{j}\cdot\mathbf{a}_{j}).$

^bOccupancy 0.50.

phosphino- and arsinobenzenechromium tricarbonyl derivatives. The first was the thermal replacement of three carbonyls from $Cr(CO)_6$ by an aryl group attached to the phosphine. Thus, refluxing the arylphosphine and chromium hexacarbonyl in a decalin solution gives rise to two series of complexes: monomeric $R_2PC_6H_5Cr(CO)_3$ and dimeric $[R_2PC_6H_5-Cr(CO)_2]_2$. This route gives low yields, requires considerable time, and is limited in scope (14). For some phosphines, such as Ph₃P and (*m*-tolyl)₃P, only the dimers are isolated (14).

The second strategy employed for the formation of $R_2PC_6H_5Cr(CO)_3$ involves the reaction of a chlorophosphine with the lithium derivative of benzenechromium tricarbonyl $(\eta^6\text{-LiC}_6H_5)Cr(CO)_3$, in THF or Et₂O, at low temperature. Two indirect routes to the lithiated intermediate have been developed; one involves a *trans*-metallation reaction between bis $(\eta^6\text{-phenyltricarbonylchromium})$ mercury and *n*-butyllithium (15). The second, more efficient, route involves *trans*-metallation of $[\eta^6\text{-(Bu}^n_3\text{Sn})\text{C}_6\text{H}_5]\text{Cr}(CO)_3$ with *n*-BuLi in THF at -78°C (16). The butyltin derivative can be synthesized by the reaction of $(\text{MeCN})_3\text{Cr}(CO)_3$ with (tributylstan-nyl)benzene.

Semmelhack et al. (17) developed a high-yield direct lithiation method involving addition of *n*-BuLi to $C_6H_6Cr(CO)_3$ in THF at -78° C in the presence of TMEDA. Subsequent addition of halophosphine or arsine affords the desired phosphinoand arsinobenzenechromium tricarbonyl derivatives. This method was adopted for the present investigation; 10 complexes (1-10) were prepared in this work including the three known compounds $Ph_2PC_6H_5Cr(CO)_3 \mathbf{1}$, $PhP[C_6H_5Cr(CO)_3]_2$ 7, and $Ph_2AsC_6H_5Cr(CO)_3$ 6, which were isolated in higher yields than previously reported (16a, 18). In our hands the yields of the $R_2P[C_6H_5Cr(CO)_3]$ phosphines are higher than those of $RP[C_6H_5Cr(CO)_3]_2$. Recrystallization is best employed as a purification method because of the possibility of decomposition of the compounds on silica gel or alumina. Compounds 1-10 are all yellow solids, except $Et_2PC_6H_5Cr(CO)_3$, 4, which is a red oily liquid; all are soluble in a range of organic solvents. In the solid state, the compounds are stable for long periods of time under an inert atmosphere. In general, their spectroscopic properties are much as expected. The ³¹P NMR shifts can be fitted reasonably well to the Grim and McFarlane equation (19): δ (w.r.t. 85% H₃PO₄) = $-62 + \Sigma \sigma^{P}$ if σ^{P} for the C₆H₅Cr(CO)₃ moiety is taken as +20.

The crystal structure of $Pr_2^iP(C_6H_5)Cr(CO)_3$ **3** is shown in Fig. 1 and selected bond lengths and bond angles appear in

Fig. 1. Molecular structure of $Pr_{2}^{i}PC_{6}H_{5}Cr(CO)_{3}$, **3**; 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.



Table 3. The "three-legged piano-stool" geometry is typical of $(\eta^{6}\text{-arene})Cr(CO)_{3}$ complexes. The CO-Cr-CO angles range from 87.6(1)° to 89.0(1)° and the Cr(CO)_{3} moiety is partially eclipsed (i.e., midway between eclipsed and staggered relative to the η^{6} -phenyl ring). A staggered structure is rare for monosubstituted arenes (20).

One of the isopropyl groups in the Pr_2^i moiety is oriented almost perpendicular to the π -arene moiety. This conformation forces the remaining isopropyl group below the plane of the π -arene ring, with the Cr(CO)₃ moiety.

The structure of $Ph_2AsC_6H_5Cr(CO)_3$, 6 (21), is very similar to that of **3**. In fact the change from Ph_2As to Pr^i_2P is barely discernible in the $C_6H_5Cr(CO)_3$ moiety. The ring C—C bonds of **3** vary between 1.391(4) and 1.419(3) Å in an apparently random manner; however, in **6** there appears to be some tendency towards an alternation in the bond lengths.

With the advent of mild synthetic routes (22), many tertiary phosphine and arsine derivatives of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ have been prepared; however, only one contains a benzene chromium tricarbonyl moiety. To fill in this gap, 10 new derivatives of Ru₃(CO)₁₂, 11, 12, 15, 16, 19, 20, 22, 23, 27, and 29 were synthesized and characterized. Most reactions employed sodium benzophenone ketyl (BPK) as catalyst. PPN salts were also used to assist the substitution reactions although this method is less satisfactory. The catalyzed reactions with the ligands $(R_2EC_6H_5)Cr(CO)_3$ $(R_2E = Me_2As, Pr^{1}2P, Et_2P, Ph_2P)$ afford the expected mono- or di-substituted products in good yield with the yields of the monosubstituted derivatives being higher. However, under the same conditions $Ph_2AsC_6H_5Cr(CO)_3$ and $PhP[C_6H_5Cr(CO)_3]_2$ yield only the monosubstituted products 27 and 29. $Bu_2^{T}PC_6H_5Cr(CO)_3$ appears to react only to a limited extent under these conditions and $PhAs[C_6H_5Cr(CO)_3]_2$ or $Bu^tP[C_6H_5Cr(CO)_3]_2$ not at all. The bulk of the ligands is probably the determining factor; however, it should be noted that the very bulky PFc_2Ph (Fc = ferrocenyl) forms $Ru_3(CO)_{10}(PFc_2Ph)_2$ in high yield (23).

Fig. 2. Molecular structure of $Ru_3(CO)_{11}[Pr^i_2PC_6H_5Cr(CO)_3]$, 15; 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.



Substitution reactions of $Os_3(CO)_{12}$ are facilitated by the use of the activated clusters, $Os_3(CO)_{11}$ (MeCN) and $Os_3(CO)_{10}$ (MeCN)₂ (24), and the new complexes **13**, **14**, **17**, **18**, **21**, **24**, **25**, **28** were prepared by using this methodology. The bulky ligands Bu'P[C₆H₅Cr(CO)₃]₂ and Bu'₂PC₆H₅Cr(CO)₃ failed to react. The trisubstituted derivative $Os_3(CO)_9[(Et_2PC_6H_5)Cr(CO)_3]_3$, **26**, was obtained by refluxing $Os_3(CO)_{11}[Et_2PC_6H_5Cr(CO)_3]$ in *n*-octane: compound **26** was the major product in addition to $Os_3(CO)_{12}$. The spectroscopic properties of the cluster derivatives are much as expected.

The crystal structures of two monosubstituted complexes 15 and 19 have been determined. ORTEP plots are shown in Figs. 2 and 3. Metrical data are summarized in Tables 3 and 4. The phosphine ligands are equatorial and the longest of the Ru— Ru bonds is *cis* to the ligand. The average metal-metal distances in 15 and 19 are 2.8908 and 2.8729 Å, respectively, which is greater than the 2.854 Å found for Ru₃(CO)₁₂. This expansion has been attributed to the bulk of the ligands. The cone angles of the isopropyl-and phenyl- phosphines are estimated to be 164° and 154°, respectively, by using data from the structure of Ru(CO)₃[Pr¹₂PC₆H₅Cr(CO)₃]².⁴

The disubstituted ruthenium cluster $\text{Ru}_3(\text{CO})_{10}$ -[$\text{Pr}^i_2\text{P}(\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3)$]₂ **16** also has been crystallographically characterized and the structure is shown in Fig. 4. Selected metrical data for the 1:1 dichloromethane solvate are listed in Tables 3 and 4.

The structure is that commonly found for $M_3(CO)_{10}L_2$ clusters where the two ligands occupy equatorial positions at opposite ends of one of the Ru—Ru bonds. The structure of

⁴ W.R. Cullen, S.J. Rettig, and H. Zhang. Unpublished results.

Table 3. Bond lengths (Å) with estimated standard deviations in parentheses.^a

Table 3.	(concluded)
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Bond	Length	Bond	Length
3			
Cr(1) - C(1)	1.835(3)	P(1)—C(10)	1.849(3)
Cr(1)—C(2)	1.819(3)	P(1)—C(13)	1.865(3)
Cr(1) - C(3)	1.834(3)	O(1)—C(1)	1.151(3)
Cr(1)—C(4)	2.231(2)	O(2)—C(2)	1.157(3)
Cr(1) - C(5)	2.209(2)	O(3) - C(3)	1.154(3)
Cr(1) - C(6)	2.206(3)	-C(4)C(5)	1.404(3)
Cr(1) - C(7)	2.218(3)	C(4)—C(9)	1.419(3)
Cr(1) - C(8)	2.211(3)	C(5)—C(6)	1.414(4)
Cr(1) - C(9)	2.197(3)	C(6)—C(7)	1.393(4)
Cr(1) - A	1.71	C(7) - C(8)	1.400(4)
P(1)—C(4)	1.840(3)	C(8)C(9)	1.391(4)
15			
Ru(1)—Ru(2)	2.9276(6)	Cr(1)—A	1.72
Ru(1)— $Ru(3)$	2.8776(5)	P(1) - C(15)	1.834(4)
Ru(1) - P(1)	2.384(1)	P(1) - C(21)	1.859(4)
Ru(1) - C(1)	1.863(4)	P(1) - C(22)	1.863(5)
Ru(1) - C(2)	1.938(5)	O(1) - C(1)	1.145(5)
Ru(1) - C(3)	1.919(5)	O(2) - C(2)	1.134(5)
Ru(2) - Ru(3)	2.8672(7)	O(3) - C(3)	1.141(5)
Ru(2) - C(8)	1.923(5)	O(4) - C(4)	1.130(5)
$R_{u}(2) = C(0)$	1.901(5)	O(5) - C(5)	1.128(5)
$R_{\rm H}(2) = C(10)$	1.945(5)	O(6) - C(6)	1.127(6)
$R_{12}(2) = C(10)$	1.921(5)	O(7) - C(7)	1.134(5)
Ru(3) - C(4)	1.921(5) 1.904(5)	O(8) - C(8)	1 134(5)
Ru(3) = C(5)	1.904(5)	O(0) - C(0)	1 129(5)
Ru(3) = C(5)	1.912(5) 1.043(5)	O(10) = C(10)	1.123(5)
Ru(3) = C(0)	1.943(5)	O(10) - O(10)	1 130(5)
$C_{r}(1) = C(12)$	1.945(5)	O(11) - WC(11)	1.150(6)
$C_{r}(1) - C(12)$	1.850(6)	O(12) - C(12) O(13) - C(13)	1.136(6)
$C_{r}(1) = C(13)$	1.830(0)	O(13) - C(13)	1.150(0)
$C_{1}(1) = C_{1}(14)$	1.030(3)	O(14) - C(14)	1.133(3)
$C_{r(1)} = C_{r(1)}$	2.274(4)	C(15) - C(10)	1.413(3)
$C_{1}(1) = C(10)$	2.207(4)	C(13) - C(20)	1.41/(0)
Cr(1) = C(17)	2.205(5)	C(10) - C(17)	1.405(0)
Cr(1) = C(18)	2.203(5)	C(17) - C(18)	1.300(0)
Cr(1) = C(19)	2.187(5)	C(18) - C(19)	1.407(7)
Cr(1) = C(20)	2.190(5)	C(19) - C(20)	1.390(0)
19 Ru(1)—Ru(2)	2 8686(6)	Cr(1)—A	1 70
Ru(1) = Ru(3)	2.8900(7)	P(1) - C(15)	1.828(5)
Ru(1) = Ru(3) Ru(1) = P(1)	2.0000(7)	P(1) = C(21)	1 840(5)
$R_{1}(1) - C(1)$	1 893(6)	P(1) = C(27)	1 838(5)
$R_{11}(1) = C(2)$	1 935(6)	O(1) - C(1)	1 120(6)
$\mathbf{R}_{1}(1) = \mathbf{C}(3)$	1.935(6)	O(2) - C(2)	1 141(6)
$\mathbf{R}_{11}(2) = \mathbf{P}_{11}(2)$	2 8602(6)	O(2) - C(2)	1 128(6)
$\operatorname{Ru}(2) = \operatorname{Ru}(3)$	2.0002(0)	O(3) - C(3)	1.130(0)
$R_{11}(2) = C(4)$	1.721(0)	O(4) - C(4)	1.123(0)
$\operatorname{Ru}(2) = \operatorname{C}(3)$	1.072(0)	O(3) - C(3)	1.140(0)
Ru(2) = C(0)	1.933(7)	O(0) - C(0)	1.119(0)
Ku(2) = C(7)	1.903(6)	O(1) - C(1)	1.124(6)
$Ru(3) \rightarrow C(8)$	1.920(6)	$O(\delta) = O(\delta)$	1.124(0)
Ku(3) = C(9)	1.941(6)	O(9) - C(9)	1.140(6)
Ku(3) - C(10)	1.902(6)	O(10) - C(10)	1.131(6)
Ku(3) = C(11)	1.932(6)	O(11) - C(11)	1.131(6)
Cr(1) - C(12)	1.843(7)	O(12) - C(12)	1.146(7)
Cr(1) - C(13)	1.854(6)	O(13) - C(13)	1.132(6)

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Bo	nd	Length	Bond	Length
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\overline{Cr(1)}$	-C(14)	1.837(6)	O(14) - C(14)	1.158(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cr(1)—	-C(15)	2.211(5)	C(15)—C(16)	1.414(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cr(1)—	-C(16)	2.199(6)	C(15)—C(20)	1.413(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cr(1)—	-C(17)	2.213(6)	C(16)—C(17)	1.392(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cr(1)-	-C(18)	2.202(6)	C(17)—C(18)	1.398(8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cr(1)	-C(19)	2.221(6)	C(18)—C(19)	1.393(8)
16 Ru(1)-Ru(1) ^b 2.8914(8) P(1)-C(9) 1.845(5) Ru(1)-Ru(2) 2.8927(6) P(1)-C(12) 1.861(4) Ru(1)-P(1) 2.384(1) P(1)-C(12) 1.851(4) Ru(1)-C(1) 1.872(4) O(1)-C(1) 1.137(5) Ru(1)-C(2) 1.905(5) O(2)-C(2) 1.133(5) Ru(1)-C(3) 1.939(5) O(3)-C(3) 1.133(5) Ru(2)-C(4) 1.903(5) O(4)-C(4) 1.137(6) Ru(2)-C(5) 1.928(5) O(5)-C(5) 1.137(6) Cr(1)-C(6) 1.843(5) O(6)-C(6) 1.448(6) Cr(1)-C(7) 1.837(5) O(7)-C(7) 1.55(6) Cr(1)-C(16) 2.197(5) C(15)-C(16) 1.411(6) Cr(1)-C(17) 2.211(5) C(16)-C(17) 1.398(8) Cr(1)-C(18) 2.214(5) C(17)-C(18) 1.405(8) Cr(1)-C(19) 2.204(5) C(18)-C(19) 1.398(8) Cr(1)-C(11) 1.884(5) P(1)-C(7) 1.826(5) Os(1)-C(11) 1.884(5) P(1)-C(1)	Cr(1)—	-C(20)	2.181(5)	C(19)—C(20)	1.410(7)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	16				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(1)-	$-\mathrm{Ru}(1)^{b}$	2.8914(8)	P(1)C(9)	1.845(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(1)-	-Ru(2)	2.8927(6)	P(1)—C(12)	1.861(4)
$\begin{array}{c cccccc} Ru(1)C(1) & 1.872(4) & O(1)C(1) & 1.137(5) \\ Ru(1)C(2) & 1.905(5) & O(2)C(2) & 1.153(5) \\ Ru(2)C(4) & 1.939(5) & O(3)C(3) & 1.133(5) \\ Ru(2)C(5) & 1.928(5) & O(5)C(5) & 1.137(6) \\ Cr(1)C(6) & 1.843(5) & O(6)C(6) & 1.148(6) \\ Cr(1)C(7) & 1.837(5) & O(7)C(7) & 1.155(6) \\ Cr(1)C(18) & 1.839(6) & O(8)C(8) & 1.146(7) \\ Cr(1)C(16) & 2.197(5) & C(15)C(16) & 1.411(6) \\ Cr(1)C(16) & 2.197(5) & C(15)C(20) & 1.427(6) \\ Cr(1)C(18) & 2.214(5) & C(16)C(17) & 1.399(7) \\ Cr(1)C(18) & 2.214(5) & C(16)C(17) & 1.399(7) \\ Cr(1)C(18) & 2.214(5) & C(16)C(19) & 1.398(8) \\ Cr(1)C(20) & 2.212(5) & C(18)C(19) & 1.398(8) \\ Cr(1)C(20) & 2.212(5) & C(19)C(20) & 1.392(7) \\ Cr(1)A & 1.71 & & & & & & & & & & & & & & & & & & &$	Ru(1)-	-P(1)	2.384(1)	P(1) - C(15)	1.851(4)
$\begin{array}{c cccccc} Ru(1)C(2) & 1.905(5) & O(2)C(2) & 1.153(5) \\ Ru(1)C(3) & 1.939(5) & O(3)C(3) & 1.133(5) \\ Ru(2)C(4) & 1.903(5) & O(4)C(4) & 1.137(6) \\ Ru(2)C(5) & 1.928(5) & O(5)C(5) & 1.137(6) \\ Cr(1)C(6) & 1.843(5) & O(6)C(6) & 1.148(6) \\ Cr(1)C(7) & 1.837(5) & O(7)C(7) & 1.155(6) \\ Cr(1)C(18) & 1.839(6) & O(8)C(8) & 1.146(7) \\ Cr(1)C(16) & 2.197(5) & C(15)C(16) & 1.411(6) \\ Cr(1)C(16) & 2.197(5) & C(15)C(20) & 1.427(6) \\ Cr(1)C(17) & 2.211(5) & C(16)C(17) & 1.399(7) \\ Cr(1)C(18) & 2.214(5) & C(17)C(18) & 1.405(8) \\ Cr(1)C(19) & 2.204(5) & C(18)C(19) & 1.398(8) \\ Cr(1)C(20) & 2.212(5) & C(18)C(19) & 1.398(8) \\ Cr(1)C(20) & 2.212(5) & C(19)C(20) & 1.392(7) \\ Cr(1)A & 1.71 & & & & & & & & & & & & & & & & & & &$	Ru(1)	-C(1)	1.872(4)	O(1) - C(1)	1.137(5)
$\begin{array}{c cccccc} Ru(1)C(3) & 1.939(5) & O(3)C(3) & 1.133(5) \\ Ru(2)C(4) & 1.903(5) & O(4)C(4) & 1.137(6) \\ Ru(2)C(5) & 1.928(5) & O(5)C(5) & 1.137(6) \\ Cr(1)C(6) & 1.843(5) & O(6)C(6) & 1.148(6) \\ Cr(1)C(7) & 1.837(5) & O(7)C(7) & 1.155(6) \\ Cr(1)C(18) & 1.839(6) & O(8)C(8) & 1.146(7) \\ Cr(1)C(16) & 2.197(5) & C(15)C(16) & 1.411(6) \\ Cr(1)C(16) & 2.197(5) & C(15)C(20) & 1.427(6) \\ Cr(1)C(16) & 2.197(5) & C(15)C(20) & 1.427(6) \\ Cr(1)C(18) & 2.214(5) & C(16)C(17) & 1.399(7) \\ Cr(1)C(18) & 2.214(5) & C(17)C(18) & 1.405(8) \\ Cr(1)C(19) & 2.204(5) & C(18)C(19) & 1.398(8) \\ Cr(1)C(20) & 2.212(5) & C(19)C(20) & 1.392(7) \\ Cr(1)A & 1.71 & & & & & & & & & & & & & & & & & & &$	Ru(1)-	-C(2)	1.905(5)	O(2)—C(2)	1.153(5)
$\begin{array}{c ccccc} Ru(2) & -C(4) & 1.903(5) & O(4) - C(4) & 1.137(6) \\ Ru(2) - C(5) & 1.928(5) & O(5) - C(5) & 1.137(6) \\ Cr(1) - C(6) & 1.843(5) & O(6) - C(6) & 1.148(6) \\ Cr(1) - C(7) & 1.837(5) & O(7) - C(7) & 1.155(6) \\ Cr(1) - C(8) & 1.839(6) & O(8) - C(8) & 1.146(7) \\ Cr(1) - C(15) & 2.251(4) & C(15) - C(16) & 1.411(6) \\ Cr(1) - C(16) & 2.197(5) & C(15) - C(20) & 1.427(6) \\ Cr(1) - C(17) & 2.211(5) & C(16) - C(17) & 1.399(7) \\ Cr(1) - C(18) & 2.214(5) & C(17) - C(18) & 1.405(8) \\ Cr(1) - C(19) & 2.204(5) & C(18) - C(19) & 1.398(8) \\ Cr(1) - C(20) & 2.212(5) & C(18) - C(19) & 1.398(8) \\ Cr(1) - C(20) & 2.212(5) & C(19) - C(20) & 1.392(7) \\ Cr(1) - A & 1.71 & & & & & & & & & & & & & & & & & & &$	Ru(1)-	-C(3)	1.939(5)	O(3)—C(3)	1.133(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ru(2)—	-C(4)	1.903(5)	O(4)—C(4)	1.137(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ru(2)—	-C(5)	1.928(5)	O(5)C(5)	1.137(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cr(1)—	-C(6)	1.843(5)	O(6)—C(6)	1.148(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cr (1)—	-C(7)	1.837(5)	O(7)—C(7)	1.155(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cr(1)—	-C(8)	1.839(6)	O(8)—C(8)	1.146(7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cr(1)—	-C(15)	2.251(4)	C(15)—C(16)	1.411(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cr(1)—	-C(16)	2.197(5)	C(15)—C(20)	1.427(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cr(1)—	-C(17)	2.211(5)	C(16)—C(17)	1.399(7)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cr(1)—	-C(18)	2.214(5)	C(17)C(18)	1.405(8)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cr(1)—	-C(19)	2.204(5)	C(18)—C(19)	1.398(8)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cr(1)	-C(20)	2.212(5)	C(19)—C(20)	1.392(7)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cr(1)—	-A	1.71		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	26				
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Os(1)-	$-Os(1)^{c}$	2.9013(3)	P(1)—C(1)	1.831(4)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Os(1)-	-P(1)	2.344(1)	P(1)—C(7)	1.826(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Os(1)-	-C(11)	1.884(5)	P(1)—C(9)	1.829(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Os(1)-	-C(12)	1.954(5)	O(1)C(11)	1.148(5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Os(1)-	-C(13)	1.918(5)	O(2)—C(12)	1.144(5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cr(1)	-C(1)	2.263(4)	O(3)—C(13)	1.162(5)
$\begin{array}{ccccccc} Cr(1) & -C(3) & 2.207(5) & O(5)C(15) & 1.149(6) \\ Cr(1) & -C(4) & 2.209(5) & O(6)C(16) & 1.149(6) \\ Cr(1) & -C(5) & 2.210(5) & C(1)C(2) & 1.414(6) \\ Cr(1) & -C(6) & 2.222(5) & C(1)C(6) & 1.429(6) \\ Cr(1) & -C(14) & 1.837(6) & C(2)C(3) & 1.415(7) \\ Cr(1) & -C(15) & 1.837(5) & C(3)C(4) & 1.387(8) \\ Cr(1) & -C(16) & 1.853(6) & C(4)C(5) & 1.401(8) \\ Cr(1) & -A & 1.72 & C(5)C(6) & 1.394(7) \\ \end{array}$	Cr(1)-	-C(2)	2.233(5)	O(4)C(14)	1.152(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cr(1)—	-C(3)	2.207(5)	O(5)—C(15)	1.149(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cr(1)—	-C(4)	2.209(5)	O(6)—C(16)	1.149(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cr(1)—	-C(5)	2.210(5)	C(1)—C(2)	1.414(6)
$\begin{array}{ccccccc} Cr(1) & -C(14) & 1.837(6) & C(2)C(3) & 1.415(7) \\ Cr(1)C(15) & 1.837(5) & C(3)C(4) & 1.387(8) \\ Cr(1)C(16) & 1.853(6) & C(4)C(5) & 1.401(8) \\ Cr(1)A & 1.72 & C(5)C(6) & 1.394(7) \\ \end{array}$	Cr(1)—	-C(6)	2.222(5)	C(1)—C(6)	1.429(6)
$\begin{array}{cccc} Cr(1) & -C(15) & 1.837(5) & C(3) - C(4) & 1.387(8) \\ Cr(1) - C(16) & 1.853(6) & C(4) - C(5) & 1.401(8) \\ Cr(1) - A & 1.72 & C(5) - C(6) & 1.394(7) \end{array}$	Cr(1)—	-C(14)	1.837(6)	C(2)C(3)	1.415(7)
$\begin{array}{cccc} Cr(1) & -C(16) & 1.853(6) & C(4) & -C(5) & 1.401(8) \\ Cr(1) & A & 1.72 & C(5) & -C(6) & 1.394(7) \end{array}$	Cr(1)—	-C(15)	1.837(5)	C(3)—C(4)	1.387(8)
Cr(1)—A 1.72 C(5)—C(6) 1.394(7)	Cr(1)	-C(16)	1.853(6)	C(4)—C(5)	1.401(8)
	Cr(1)	-A	1.72	C(5)—C(6)	1.394(7)

"Here and elsewhere, A refers to the unweighted centroid of the

 η^6 -coordinated aromatic ring.

^bSymmetry operation: x, y, z. ^cSymmetry operation: 1 - y, x - y, z.

 $Os_3(CO)_{10}(PFc_2Ph)_2$ provides a rare example of the alternative 1,2-*trans,cis* arrangement of the phosphine ligands (25). In **16** the three Ru—Ru bond distances (mean value 2.8923 Å) are the same within experimental error. This is in contrast to the monosubstituted complexes **15** and **19** in which there are significant differences in the three Ru—Ru separations with the Ru—Ru bond *cis* to the phosphine ligand being significantly elongated. In other disubstituted complexes, Ru₃(CO)₁₀L₂, the

Table 4. Bond angles (deg) with estimated standard deviations in parentheses.^a

Bonds	Angle (deg)	Bonds	Angle (deg)
3			
C(1)-Cr(1)-C(2)	89.0(1)	C(10)-P(1)-C(13)	103.3(1)
C(1)-Cr(1)-C(3)	87.6(1)	Cr(1)-C(1)-O(1)	178.3(3)
C(1)-Cr(1)-A	126.5	Cr(1)-C(2)-O(2)	178.7(3)
C(2)-Cr(1)-C(3)	87.6(1)	Cr(1)-C(3)-O(3)	177.8(3)
C(2)-Cr(1)-A	125.9	P(1)-C(4)-C(5)	125.5(2)
C(3)-Cr(1)-A	127.5	P(1)-C(4)-C(9)	116.3(2)
C(4)-P(1)-C(10)	105.2(1)	C(5)-C(4)-C(9)	117.2(2)
C(4)-P(1)-C(13)	98.5(1)		
15			
Ru(2)-Ru(1)-Ru(3)	59.19(1)	Ru(2)-Ru(3)-C(6)	90.0(2)
Ru(2)-Ru(1)-P(1)	115.89(3)	Ru(2)-Ru(3)-C(7)	89.9(1)
Ru(2)-Ru(1)-C(1)	143.7(1)	C(4)-Ru(3)-C(5)	99.6(2)
Ru(2)-Ru(1)-C(2)	86.7(1)	C(4)-Ru(3)-C(6)	92.8(2)
Ru(2)-Ru(1)-C(3)	93.3(1)	C(4)-Ru(3)-C(7)	92.7(2)
Ru(3)-Ru(1)-P(1)	174.27(3)	C(5)-Ru(3)-C(6)	90.7(2)
Ru(3)-Ru(1)-C(1)	84.8(1)	C(5)-Ru(3)-C(7)	88.1(2)
Ru(3)-Ru(1)-C(2)	93.0(1)	C(6)-Ru(3)-C(7)	174.5(2)
Ru(3)-Ru(1)-C(3)	89.6(1)	C(12)-Cr(1)-C(13)	87.1(2)
P(1)-Ru(1)-C(1)	100.3(1)	C(12)-Cr(1)-C(14)	85.9(2)
P(1)-Ru(1)-C(2)	89.6(1)	C(12)-Cr(1)-A	131.7
P(1)-Ru(1)-C(3)	87.8(1)	C(13)-Cr(1)-C(14)	87.6(2)
C(1)-Ru(1)-C(2)	91.6(2)	C(13)-Cr(1)-A	126.6
C(1)-Ru(1)-C(3)	90.2(2)	C(14)-Cr(1)-A	123.9
C(2)-Ru(1)-C(3)	177.0(2)	Ru(1)-P(1)-C(15)	120.6(1)
Ru(1)-Ru(2)-Ru(3)	59.54(1)	Ru(1)-P(1)-C(21)	113.6(1)
Ru(1)-Ru(2)-C(8)	152.7(1)	Ru(1)-P(1)-C(22)	114.5(1)
Ru(1)-Ru(2)-C(9)	109.6(1)	C(15)-P(1)-C(21)	104.2(2)
Ru(1)-Ru(2)-C(10)	91.4(1)	C(15)-P(1)-C(22)	98.7(2)
Ru(1)-Ru(2)-C(11)	82.2(1)	C(21)-P(1)-C(22)	102.7(2)
Ru(3)-Ru(2)-C(8)	93.6(1)	Ru(1)-C(1)-O(1)	176.7(4)
Ru(3)-Ru(2)-C(9)	169.0(1)	Ru(1)-C(2)-O(2)	173.2(4)
Ru(3)-Ru(2)-C(10)	89.1(1)	Ru(1)-C(3)-O(3)	173.4(4)
Ru(3)-Ru(2)-C(11)	88.8(1)	Ru(3)-C(4)-O(4)	178.5(4)
Ru(8)-Ru(2)-C(9)	97.3(2)	Ru(3)-C(5)-O(5)	176.0(5)
Ru(8)-Ru(2)-C(10)	93.3(2)	Ru(3)-C(6)-O(6)	173.3(5)
Ru(8)-Ru(2)-C(11)	93.0(2)	Ru(3)-C(7)-O(7)	172.5(4)
Ru(9)-Ru(2)-C(10)	89.5(2)	Ru(2)-C(8)-O(8)	177.4(4)
Ru(9)-Ru(2)-C(11)	91.3(2)	Ru(2)-C(9)-O(9)	176.9(4)
C(10)-Ru(2)-C(11)	173.4(2)	Ru(2)-C(10)-O(10)	173,4(4)
Ru(1)-Ru(3)-Ru(2)	61.28(1)	Ru(2)-C(11)-O(11)	172.6(4)
Ru(1)-Ru(3)-C(4)	154.7(1)	Cr(1)-C(12)-O(12)	176.9(5)
Ru(1)-Ru(3)-C(5)	105.7(2)	Cr(1)-C(13)-O(13)	177.3(5)
Ru(1)-Ru(3)-C(6)	86.6(1)	Cr(1)-C(14)-O(14)	177.6(5)
Ru(1)-Ru(3)-C(7)	88.5(1)	P(1)-C(15)-C(16)	118.3(3)
Ru(2)- $Ru(3)$ - $C(4)$	93 5(1)	P(1)-C(15)-C(20)	1232(3)
Ru(2)-Ru(3)-C(5)	166.8(2)	C(16-C(15)-C(20)	117.2(4)
19			
Ru(2)-Ru(1)-Ru(3)	59.56(2)	Ru(2)-Ru(3)-C(10)	170.4(2)
Ru(2)-Ru(1)-P(1)	158.58(4)	Ru(2)-Ru(3)-C(11)	90.7(2)
Ru(2)-Ru(1)-C(1)	94.3(2)	C(8)-Ru(3)-C(9)	94.6(2)
Ru(2)-Ru(1)-C(2)	91.4(2)	C(8)-Ru(3)-C(10)	99.7(2)
		$C(9) P_{11}(2) C(11)$	02 5(2)
Ru(2)-Ru(1)-C(3)	88.2(2)		77
Ru(2)-Ru(1)-C(3) Ru(3)-Ru(1)-P(1)	88.2(2) 99.06(4)	C(8)-Ru(3)- $C(11)$	92.3(2) 87 7(2)
Ru(2)-Ru(1)-C(3) Ru(3)-Ru(1)-P(1) Ru(3)-Ru(1)-C(1)	88.2(2) 99.06(4) 153.8(2)	C(8)-Ru(3)-C(11) C(9)-Ru(3)-C(10) C(9)-Ru(3)-C(11)	87.7(2) 172 9(2)

Table 4.	(continued))
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Bonds	Angle (deg)	Bonds	Angle (deg)
Ru(3)-Ru(1)-C(3)	90.2(2)	C(12)-Cr(1)-C(13)	88.7(3)
P(1)-Ru(1)-C(1)	107.1(2)	C(12)-Cr(1)-C(14)	85.4(3)
P(1)-Ru(1)-C(2)	88.0(2)	C(12)-Cr(1)-A	128.0
P(1)-Ru(1)-C(3)	93.6(2)	C(13)-Cr(1)-C(14)	89.2(3)
C(1)-Ru(1)-C(2)	89.1(2)	C(13)-Cr(1)-A	126.7
C(1)-Ru(1)-C(3)	87.5(2)	C(14)-Cr(1)-A	125.7
C(2)-Ru(1)-C(3)	176.5(2)	Ru(1)-P(1)-C(15)	117.3(2)
Ru(1)-Ru(2)-Ru(3)	60.59(2)	Ru(1)-P(1)-C(21)	112.7(2)
Ru(1)-Ru(2)-C(4)	162.6(2)	Ru(1)-P(1)-C(27)	118.7(2)
Ru(1)-Ru(2)-C(5)	97.5(2)	C(15)-P(1)-C(21)	99.6(2)
Ru(1)-Ru(2)-C(6)	87.1(2)	C(15)-P(1)-C(27)	101.9(2)
Ru(1)-Ru(2)-C(7)	90.4(2)	C(21)-P(1)-C(27)	104.0(2)
Ru(3)-Ru(2)-C(4)	102.1(2)	Ru(1)-C(1)-O(1)	175.8(6)
Ru(3)-Ru(2)-C(5)	158.0(2)	Ru(1)-C(2)-O(2)	172.4(5)
$R_{U}(3)$ - $R_{U}(2)$ - $C(6)$	87 7(2)	$R_{II}(1)$ - $C(3)$ - $O(3)$	172.7(5)
Ru(3)-Ru(2)-C(7)	88 1(2)	Ru(2)-C(4)-O(4)	177.2(6)
C(4)-Ru(2)-C(5)	99 9(3)	Ru(2) - C(5) - O(5)	179 1(6)
C(4)-Ru(2)-C(6)	90.9(3)	Ru(2) - C(6) - O(6)	174 6(5)
C(4)-Ru(2)-C(7)	90.5(2)	Ru(2) = C(0) = O(0) Ru(2) = C(0) = O(0)	173.0(5)
C(5)-Ru(2)-C(6)	92.9(2)	Ru(3)-C(8)-O(8)	179.6(5)
C(5)-Ru(2)-C(7)	90.7(2)	Ru(3)-C(9)-O(9)	171.8(5)
C(6)-Ru(2)-C(7)	175 8(2)	Ru(3) - C(10) - O(10)	175.8(5)
$R_{1}(1) - R_{1}(3) - R_{1}(2)$	59.85(1)	Ru(3)-C(11)-O(11)	172 7(5)
$R_{1}(1) - R_{1}(3) - C(8)$	1/10 6(2)	Cr(1)-C(12)-O(12)	178.0(6)
$R_{u}(1) = R_{u}(3) - C(0)$	87.0(2)	Cr(1) - C(12) - O(12)	178.4(6)
$R_{u}(1) \cdot R_{u}(3) \cdot C(10)$	110.7(2)	$C_r(1) - C(13) - O(13)$	178.6(6)
Ru(1) - Ru(3) - C(10)	$\frac{110.7(2)}{86.4(2)}$	P(1) C(14) - O(14)	173.0(0) 121.7(4)
Ru(1)- $Ru(3)$ - $C(11)$	80.4(2)	P(1) - C(15) - C(10) P(1) - C(15) - C(20)	121.7(4) 120 5(4)
Ru(2) - Ru(3) - C(0)	09.0(2) 00.1(2)	$\Gamma(1)$ - $C(13)$ - $C(20)$	120.3(4) 117.5(5)
$\operatorname{Ku}(2)$ - $\operatorname{Ku}(3)$ - $\operatorname{C}(3)$	90.1(2)	C(10)-C(13)-C(20)	117.3(3)
16 D (1)h D (1) D (2)			0.7.6(0)
$\operatorname{Ru}(1)^{\circ}$ - $\operatorname{Ru}(1)$ - $\operatorname{Ru}(2)$	60.014(9)	C(6)-Cr(1)-C(7)	87.6(2)
$Ru(1)^{\nu}-Ru(1)-P(1)$	174.92(3)	C(6)-Cr(1)-C(8)	87.8(3)
$Ru(1)^{\nu}-Ru(1)-C(1)$	86.1(1)	C(6)-Cr(1)-A	126.5
$Ru(1)^{\nu}-Ru(1)-C(2)$	93.2(1)	C(7)-Cr(1)-C(8)	85.9(2)
$Ru(1)^{\nu}-Ru(1)-C(3)$	82.0(1)	C(7)-Cr(1)-A	130.2
Ru(2)-Ru(1)-P(1)	119.81(3)	C(8)-Cr(1)-A	125.1
Ru(2)-Ru(1)-C(1)	139.8(2)	Ru(1)-P(1)-C(9)	119.3(1)
Ru(2)-Ru(1)-C(2)	69.8(1)	Ru(1)-P(1)-C(12)	112.1(1)
Ru(2)-Ru(1)-C(3)	97.6(1)	Ru(1)-P(1)-C(15)	117.7(1)
P(1)-Ru(1)-C(1)	95.9(1)	C(9)-P(1)-C(12)	102.6(2)
P(1)-Ru(1)-C(2)	91.4(1)	C(9)-P(1)-C(15)	102.3(2)
P(1)-Ru(1)-C(3)	93.1(1)	C(12)-P(1)-C(15)	100.1(2)
C(1)-Ru(1)-C(2)	93.1(2)	Ru(1)-C(1)-O(1)	174.4(5)
C(1)-Ru(1)-C(3)	98.4(2)	Ru(1)-C(2)-O(2)	170.7(5)
C(2)-Ru(1)-C(3)	167.2(2)	Ru(1)-C(3)-O(3)	178.7(4)
$\operatorname{Ru}(1)$ - $\operatorname{Ru}(2)$ - $\operatorname{Ru}(1)^b$	59.97(2)	Ru(2)-C(4)-O(4)	176.2(5)
Ru(1)-Ru(2)-C(4)	102.9(1)	Ru(2)-C(5)-O(5)	169.3(5)
$Ru(1)-Ru(2)-C(4)^{b}$	154.6(1)	Cr(1)-C(6)-O(6)	179.7(6)
Ru(1)-Ru(2)-C(5)	75.0(2)	Cr(1)-C(7)-O(7)	177.3(5)
$Ru(1)-Ru(2)-C(5)^{b}$	98.0(2)	Cr(1)-C(8)-O(8)	178.4(6)
$C(4)-Ru(2)-C(4)^{b}$	98.8(3)	P(1)-C(15)-C(16)	118.9(3)
C(4)-Ru(2)-C(5)	94.8(2)	P(1)-C(15)-C(20)	123.8(3)
$C(4)-Ru(2)-C(5)^{b}$	90.3(2)	C(16)-C(15)-C(20)	116.7(4)
$C(5)-Ru(2)-C(5)^{b}$	172.0(3)		
76			
Δv $\Omega_{s}(1)^{c} \Omega_{s}(1) \Omega_{s}(1)^{d}$	60.00	$C(14) C_r(1) A$	124 8
$O_{S(1)} - O_{S(1)} - O_{S(1)}$	00.00	C(1+)-CI(1)-A	124.0

 Table 4. (concluded).

Bonds	Angle (deg)	Bonds	Angle (deg)
$Os(1)^{c}-Os(1)-P(1)$	164.42(3)	C(15)-Cr(1)-A	125.2
$Os(1)^{c}-Os(1)-C(11)$	102.1(1)	C(16)-Cr(1)-A	130.9
$Os(1)^{c}-Os(1)-C(12)$	78.0(1)	Os(1)-P(1)-C(1)	116.1(1)
$Os(1)^{c}-Os(1)-C(13)$	97.0(1)	Os(1)-P(1)-C(7)	111.3(2)
$Os(1)^{d}-Os(1)-P(1)$	110.63(3)	Os(1)-P(1)-C(9)	114.5(2)
$Os(1)^{d}-Os(1)-C(11)$	154.5(1)	C(1)-P(1)-C(7)	105.7(2)
$Os(1)^{d}-Os(1)-C(12)$	96.1(1)	C(1)-P(1)-C(9)	103.6(2)
$Os(1)^{d}-Os(1)-C(13)$	72.8(1)	C(7)-P(1)-C(9)	104.5(2)
P(1)-Os(1)-C(11)	90.5(1)	P(1)-C(1)-C(2)	120.5(3)
P(1)-Os(1)-C(12)	91.4(1)	P(1)-C(1)-C(6)	120.9(3)
P(1)-Os(1)-C(13)	91.2(1)	C(2)-C(1)-C(6)	118.1(4)
C(11)-Os(1)-C(12)	97.5(2)	Os(1)-C(11)-O(1)	173.5(4)
C(11)-Os(1)-C(13)	93.3(2)	Os(1)-C(12)-O(2)	175.8(4)
C(12)-Os(1)-C(13)	168.8(2)	Os(1)-C(13)-O(3)	173.9(4)
C(14)-Cr(1)-C(15)	88.6(2)	Cr(1)-C(14)-O(4)	178.2(5)
C(14)-Cr(1)-C(16)	87.9(2)	Cr(1)-C(15)-O(5)	178.9(5)
C(15)-Cr(1)-C(16)	86.2(2)	Cr(1)-C(16)-O(6)	176.7(5)

"Here and elsewhere, A refers to the unweighted centroid of the $\eta^6\mbox{-}coordinated$ aromatic ring.

^bSymmetry operation: x, y, z.

Symmetry operation: 1 - y, x - y, z.

^dSymmetry operation: 1 - x + y, 1 - x, z.

Fig. 3. Molecular structure of $Ru_3(CO)_{11}[Ph_2PC_6H_5Cr(CO)_3]$, 19; 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.



Fig. 4. Molecular structure of $Ru_3(CO)_{10}[Pr^i_2PC_6H_5Cr(CO)_3)]_2$, **16**; 33% probability thermal ellipsoids are shown for the non-hydrogen atoms.







 M_3 frame is essentially an isosceles triangle (26). The average Ru—Ru bond distance in **16** is longer than that in the parent carbonyl (mean 2.854 Å) by 0.04 Å and is not significantly different from that in the monosubstituted complex **15** (mean 2.8908 Å).

In 16 the introduction of two phosphine ligands results in considerable twisting of the RuL'₄ units about the Ru—Ru bonds. Unlike the monosubstituted complexes, none of the equatorial carbonyls are found on the Ru₃ plane; for example, CO(1) and CO(4) lie on opposite sides of the Ru₃ plane by 0.73 Å and 0.64 Å, respectively. As a result, all the axial carbonyls are also moved from their idealized positions. Consequently there are no pronounced differences in the bond distances between axial carbonyls and equatorial carbonyls (mean 1.911 Å); the pseudoequatorial Ru—CO(1) bond at the substituted ruthenium atom is the shortest (1.872(4) Å).

The molecular structure of the trisubstituted derivative $Os_3(CO)_9[Et_2PC_6H_5Cr(CO)_3]_3$ **26** has been determined. The relevant bond distances and angles are tabulated in Tables 3 and 4 and an ORTEP plot of the structure is shown in Fig. 5. The molecule **26** has a crystallographic threefold axis, and the structure contains an equilateral triangular Os_3 core with the three phosphine ligands bound one to each osmium atom in pseudo-equatorial sites. The Os-Os bond distances are identical at 2.9013(3) Å and are longer than those in the parent car-

bonyl (average 2.877 Å (27)), by 0.024 Å. In $Os_3(CO)_9(PPh_3)_3$ the average Os—Os bond distance is also increased to 2.91 Å, but in trisubstituted ruthenium clusters the average Ru—Ru separation is essentially the same as that found in $Ru_3(CO)_{12}$ (28).

In 26 the phosphorus atoms are coordinated at pseudo-equatorial sites and are all situated away from the Os_3 plane by 0.52 Å in the same direction. The Os—P bond at 2.344(1) Å is surprisingly shorter than the Ru—P bond found in 19 (2.372(1) Å) and 15 (2.384(1) Å). In some other trisubstituted complexes the phosphine ligands are arranged in such a way that one lies below the M₃ plane, while the other two lie above it (28).

The products of the thermal decomposition of some of these cluster complexes will be reported in a forthcoming publication (29).

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References

 M.A. Bennet and H.P. Schwemln. Angew. Chem. Int. Ed. Engl. 28, 1296 (1989).

- W.R. Cullen, S.J. Rettig, and T.-C. Zheng. Organometallics, 11, 928 (1992).
- W.R. Cullen, S.J. Rettig, and T.-C. Zheng. Organometallics, 14, 1466 (1995).
- (a) W.R. Cullen, S.J. Rettig, and H. Zhang. Organometallics, 10, 2965 (1991); (b) Organometallics, 11, 1000 (1992); (c) Organometallics, 12, 1964 (1993).
- 5. C.A.L Mahaffy and P.L. Pauson. Inorg. Synth. 19, 154 (1979).
- (a) M.I. Bruce, J.G. Matisons, R.C. Wallis, J.M. Patrick, and A.H. White. J. Chem. Soc. Dalton Trans. 2365 (1983); (b) M.I. Bruce, C.M. Jensen, and N.L. Jones. Inorg. Synth. 28, 216 (1990).
- B.F.G. Johnson, J. Lewis, and D.A. Pippard. J. Chem. Soc. Dalton Trans. 407 (1981).
- 8. E. Roberts, E.E. Turner, and F. W. Bury. J. Chem. Soc. 1443 (1926).
- 9. M. Fild, O. Stelzer, and R. Schmutzler. Inorg. Synth. 14, 4 (1973).
- 10. D.P. Tate, W.R. Knipple, and J.M. Augl. Inorg. Chem. 1, 433 (1962).
- 11. G.A. Foulds, B.F.G. Johnson, and J. Lewis. J. Organomet. Chem. 296, 147, (1985).
- 12. M.I. Bruce, J.G. Matisons, and B.K. Nicholson. J. Organomet. Chem. 247, 321 (1983).
- (a) International tables for X-ray crystallography. Vol. IV. Kynoch Press. Birmingham, U.K. (present distributor Kluwer Academic Publishers, Boston, Mass, U.S.A.). 1974. pp. 99–102;
 (b) International tables for crystallography. Vol. C. Kluwer Academic Publishers, Boston, Mass, U.S.A. 1992. pp. 200–206.
- 14. J.A. Bowden and R. Colton. Aust. J. Chem. 24, 2471 (1971).
- 15. M.D. Rausch and R.E. Gloth. J. Organomet. Chem. 153, 59 (1978).
- (a) M.E. Wright. Organometallics, 8, 407 (1989); (b) M.E. Wright, L. Lawson, R.T. Baker, and D.C. Roe. Polyhedron, 11, 323 (1992).
- M.F. Semmelhack, J. Bisaha, and M. Czarny, J. Am. Chem. Soc. 101, 768 (1979).

- (a) H.J. Wasserman, M.J. Wovkulich, J.D. Atwood, and M.R. Churchill. Inorg. Chem. 19, 2831 (1980); (b) M.D. Rausch and R.E. Gloth. J. Organomet. Chem. 153, 59 (1978).
- 19. S.O. Grim and W. McFarlane. Nature, 208, 995 (1965).
- J. Li, A.D. Hunter, S.G. Bott, and J.L. Atwood. Organometallics, **11**, 3050 (1992).
- H.J. Wasserman, M.J. Wovkulich, J.D. Atwood, and M.R. Churchill. Inorg. Chem. 19, 2831 (1980).
- (a) M. Arewgoda, B.H. Robinson, and J. Simpson. J. Chem. Soc. Chem. Commun. 284 (1982); J. Am. Chem. Soc. 105, 1893 (1983); (b)M.I. Bruce, J.G. Matisons, and B.K. Nicholson. J. Organomet. Chem. 247, 321 (1983); (c) G. Lavigne and H.D. Kaze. J. Am. Chem. Soc. 106, 4647 (1984); (d) M.O. Albers, E. Singleton, and N.J. Coville. J. Organomet. Chem. 326, 229 (1987).
- S.T. Chacon, W.R. Cullen, M.I. Bruce, O.B. Shawkataly, F.W.B. Einstein, R.H. Jones, and A.C. Willis. Can. J. Chem. 68, 2001 (1990).
- (a)B.F.G. Johnson, J. Lewis, and D.A. Pippard. J. Chem. Soc. Dalton Trans. 407 (1987); (b) B.F.G. Johnson, J. Lewis, T.I. Odiaka, and P.R. Raithby. J. Organomet. Chem. 216, C56 (1981).
- W.R. Cullen, S.J. Rettig, and T.-C. Zheng. Can. J. Chem. 70, 2329 (1992).
- M.I. Bruce, M.J. Liddell, C.A. Hughes, J.M. Patrick, B.W. Skelton, and A.H. White. J. Organomet. Chem. 347, 181 (1988).
- M.R. Churchill, F.J. Hollander, and P.J. Hutchinson. Inorg. Chem. 16, 2655 (1977).
- M.I. Bruce, M.J. Liddell, O.B. Shawkataly, C.A. Hughes, B.W. Skelton, and A.H. White. J. Organomet. Chem. 347, 207 (1988).
- 29. W.R. Cullen, S.J. Rettig, and H. Zhang. Inorg. Chim. Acta. In press.