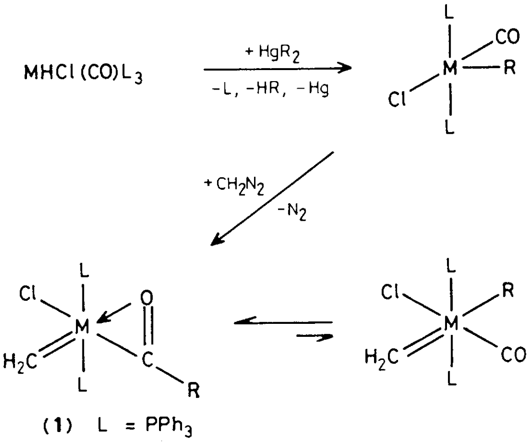
Terminal Methylene Complexes of Ruthenium(II) and Osmium(II) and Intramolecular Methylene and Acyl Ligand Combination to form Metallaoxetenes: The Crystal Structures of [OsCl(η^2-C[O]-*o*-tolyl)(=CH_2)(PPh_3)$_2$] and [$\overline{\text{Ru(=C[Ph]O}}\text{C}H_2$)(CN-*p*-tolyl)$_2$($PPh_3$)$_2$]$ClO_4$

D. Scott Bohle, George R. Clark, Clifton E. F. Rickard, Warren R. Roper,* William E. B. Shepard, and L. James Wright

Department of Chemistry, University of Auckland, Private Bag, Auckland, New Zealand

The isolable methylene complexes [MCl(η^2-C[O]R)(=CH_2)(PPh_3)$_2$] (M = Ru, R = Ph, *o*-tolyl, *p*-tolyl; M = Os, R = *o*-tolyl) which result when [MRCl(CO)(PPh_3)$_2$] is treated with diazomethane react with carbon monoxide and *p*-tolylisocyanide to form compounds with the unusual metallaoxetene, [$\overline{\text{M=C(R)O}}\text{C}H_2$], ring.

Transition metal complexes which incorporate a terminal methylene ligand have often been detected spectroscopically or implicated in reactions but very few have proved to be isolable as crystalline solids. The synthetic methods which have been utilized for the preparation of these complexes can be classified as (a) deprotonation of a cationic methyl derivative, [L_nMMe]$^+$, (b) removal of a suitable leaving group (Y) from a substituted methyl derivative, [L_nMCH_2Y], (c) photolytic reductive elimination of methane from a dimethyl derivative, [L_nMMe_2], and (d) dinitrogen loss from an intermediate diazomethane complex. Only four methylene complexes have been structurally characterized. These are [Ta(C_5H_5)$_2$(=CH_2)Me] prepared by method a,[1] [Re(C_5Me_5)(NO)(=CH_2){P(OPh)$_3$}]PF_6 (method b),[2] [$\overline{\text{Ir(=CH}_2\text{)\{N(SiMe}_2\text{CH}_2}$$PPh_2$)$_2$}] (method c),[3] and [OsCl(NO)(=CH_2)(PPh_3)$_2$] (method d).[4] Herein we report: (i) new examples of the syntheses of stable terminal methylene complexes utilizing diazomethane, (ii) the structure of one such complex [OsCl(η^2-C[O]-*o*-tolyl)(=CH_2)(PPh_3)$_2$], (**1d**), which is also the first example of an osmium complex containing an η^2-acyl ligand, (iii) substitution–addition reactions of these complexes which in certain cases lead to attack by the acyl oxygen on the methylene fragment, and (iv) the



(**1**) L = PPh_3
a; M = Ru, R = Ph
b; M = Ru, R = *o*-tolyl
c; M = Ru, R = *p*-tolyl
d; M = Os, R = *o*-tolyl

Scheme 1. Synthesis of [MCl(η^2-C[O]R)(=CH_2)(PPh_3)$_2$].

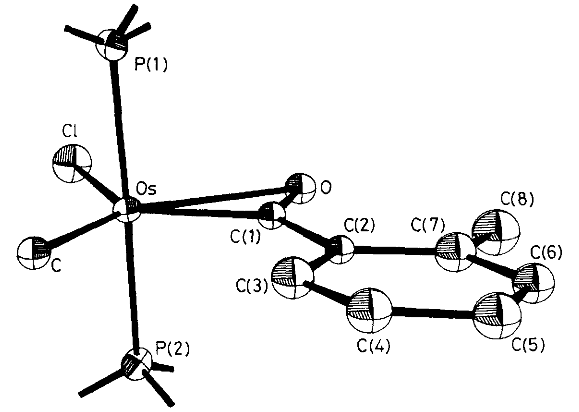
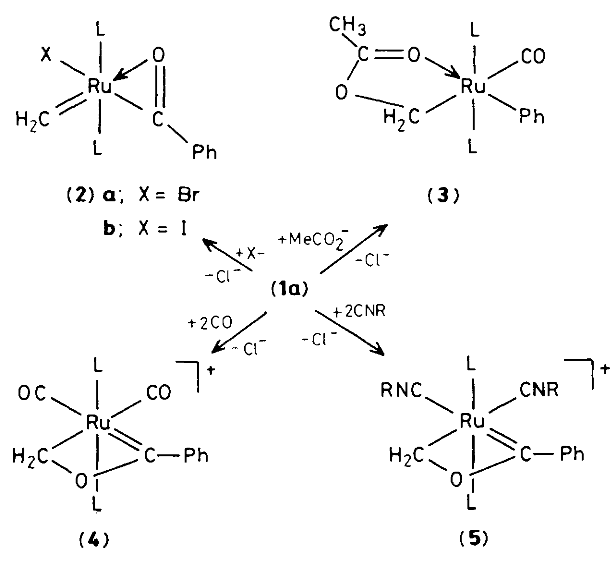


Figure 1. Molecular structure of [OsCl(η^2-C[O]-*o*-tolyl)(=CH_2)(PPh_3)$_2$] (**1d**) (phenyl rings omitted for clarity). Important bond lengths (Å) and angles (°): Os–P(1) 2.350(2), Os–C 1.856(12), Os–Cl 2.401(3), Os–C(1) 2.009(11), Os–O 2.423(9), Os–P(2) 2.356(2), C(1)–O 1.22(1), C(1)–C(2) 1.44(2); Cl–Os–O 99.7(2), Cl–Os–C(1) 129.9(4), C–Os–C(1) 109.8(5), C(1)–Os–O 30.2(4), Os–C(1)–O 94.0(7), Os–C(1)–C(2) 140.2(9), O–C(1)–C(2) 125.6(10), Os–O–C(1) 55.8(6).



Scheme 2. Reactions of [RuCl(η^2-C[O]Ph)(=CH_2)(PPh_3)$_2$]. L = PPh_3, R = *p*-tolyl, X = Br, I.

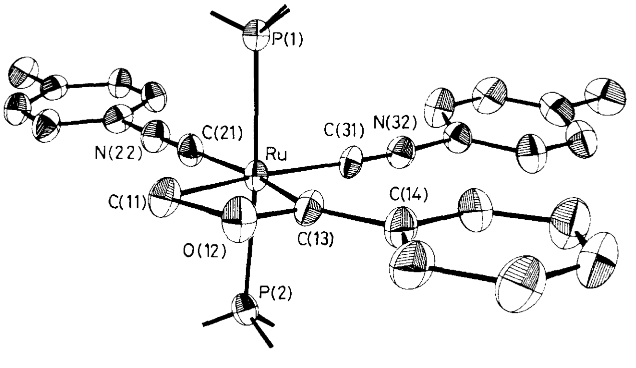


Figure 2. Molecular structure of [Ru(=C[Ph]OCH_2)(CN-*p*-tolyl)$_2$(PPh_3)$_2$]ClO_4 (**5**) (phenyl rings of triphenylphosphine omitted for clarity). Important bond lengths (Å) and angles (°): Ru–P(1) 2.370(2), Ru–C(21) 1.998(7), Ru–C(11) 2.164(6), Ru–C(13) 2.006(7), Ru–P(2) 2.366(2), Ru–C(31) 2.001(6), C(11)–O(12) 1.508(8), O(12)–C(13) 1.313(8), C(21)–N(22) 1.166(9), C(31)–N(32) 1.135(9), C(13)–C(14) 1.481(9); Ru–C(11)–O(12) 91.5(4), C(11)–O(12)–C(13) 100.6(5), O(12)–C(13)–Ru 105.2(4), Ru–C(13)–C(14) 143.2(5), O(12)–C(13)–C(14) 111.6(6), C(11)–Ru–C(13) 62.7(2)°.

structure of one such product [Ru(=C[Ph]OCH_2)(CN-*p*-tolyl)$_2$(PPh_3)$_2$]ClO_4, (**5**).

The methylene complexes (**1a**—**d**) (see Scheme 1) are prepared in 72—45% yield by treating dichloromethane solutions of co-ordinatively unsaturated aryl complexes,[5] MRCl(CO)(PPh_3)$_2$, with a diethyl ether solution of diazomethane. For successful reaction it is important that the diazomethane solution (*ca.* 5 fold excess, *ca.* 0.2 M) is added slowly at room temperature.† Note that the osmium substrates with R = phenyl or *p*-tolyl did not yield methylene complexes by employing this procedure. The light yellow complexes (**1a**—**d**) are air stable solids that decompose only slowly in solution at room temperature. The only other reported instance where reaction with diazomethane leads to an isolable terminal methylene complex involves a d^8 Os^0 nitrosyl.[4] It may be significant that both OsCl(NO)(PPh_3)$_2$ and MRCl(CO)(PPh_3)$_2$ can accommodate η^2-co-ordination of diazomethane as a 1,3-dipole, the former through bending of the nitrosyl and the latter through a migratory insertion to give a σ-acyl complex.

The crystal structure‡ of (**1d**) (Figure 1) confirms that the methylene and the carbon of the η^2-acyl are *cis* to one another in a highly distorted octahedral geometry [Cl–Os–CH_2 = 120.3(4)°]. The methylene hydrogen atoms have not been located and it is therefore not possible to determine the orientation of the CH_2 plane. The osmium–methylene bond length is at the short end of the range (1.90—1.97 Å) found for related carbene[6] and vinylidene[7] complexes. In solution, equilibrium between the η^2-acyl and carbonyl–aryl form is suggested by the presence of a weak terminal ν(CO) absorption. This band is most intense when the anionic ligands for (**1**) are X = Cl and R = Ph and least intense when X = I and R = *o*-tolyl. This situation parallels the rapid η^2-acyl/carbonyl–aryl equilibrium found in solution for [RuRCl(CO)$_2$(PPh_3)$_2$].[5]

Facile halide metathesis (10 min, 25 °C, excess of LiBr or

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† New compounds (**1**)—(**5**) have all given satisfactory elemental analyses. Important i.r. absorptions (cm^{-1}): (**1a**) 1542, 1207, 885 (η^2-C[O]Ph); (**1b**) 1540, 1187, 892 (η^2-C[O]-*o*-tolyl); (**1c**) 1536, 1168, 900 (η^2-C[O]-*p*-tolyl); (**1d**) 1506, 1196, 904 (η^2-C[O]-*o*-tolyl); (**2a**) 1543, 1207, 886 (η^2-C[O]Ph); (**2b**) 1540, 1212, 898 (η^2-C[O]Ph); (**3**) 1891, 1845 (CO), 1622, 1364, 1184, 802 (η^2-CH_2OC[O]Me); (**4**) 2054, 1994, (CO), 1348, 1309, 1256, 944 (η^2-=C[Ph]OCH_2); (**5**) 2126, 2088, 2033, (CNR), 1337, 1305, 1252, 942 (η^2-=C[Ph]OCH_2). N.m.r. data for (**1d**): ^1H ($CDCl_3$, 300 K) δ 16.94 [t, CH_2, *J*(PH) 13.64 Hz]. $^{13}C\{^1H\}$($CDCl_3$, 300 K), δ 248.8 [t, CH_2, *J*(PC) 6.5 Hz].

‡ *Crystal data* for (**1d**) $C_{45}H_{39}ClOOsP_2$, M = 882.65, orthorhombic, $Pca2_1$, a = 24.346(3), b = 9.632(1), c = 15.716(4) Å, U = 3685.4 Å^3, D_c = 1.591 g cm^{-1} for Z = 4, $F(000)$ = 1760, λ(Mo-K_α) = 0.71069 Å, μ(Mo-K_α) = 38.6 cm^{-1}. 2615 observed data [$I > 3\sigma(I)$] were collected at −150 °C on a Nicolet diffractometer. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares to R = 0.039, R_w = 0.039.

Crystal data for (**5**) (dichloromethane solvate): $C_{61}H_{53}Cl_3N_2O_5P_2Ru$, M = 1163.52, monoclinic, $P2_1/n$, a = 14.871(3), b = 19.534(3), c = 18.601(4) Å, β = 97.07°, U = 5362.31 Å^3, D_c = 1.400 g cm^{-3}, for Z = 4, $F(000)$ = 2392, λ(Mo-K_α) = 0.71069 Å, μ(MoK_α) = 5.3 cm^{-1}, 6545 observed data [$I > 3\sigma(I)$] were collected at −140 °C on a Nicolet diffractometer. The structure was solved as for (**1d**), R = 0.067, R_w = 0.076.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

LiI) results in substitution of bromide or iodide for the chloride in (**1a**) to give (**2**) (Scheme 2). Acetate also substitutes for the chloride in (**1a**), but the isolated product, $[\overline{\mathrm{Ru(CH_2OC[O}}\mathrm{]Me)Ph(CO)(PPh_3)_2}]$, (**3**), is the result of acetate oxygen addition to methylene leading to a η^2-acetatomethyl ligand. This is accompanied by migration of the phenyl of the η^2-phenylacyl ligand to the metal. Under mild carbonylation conditions (300 kPa of CO, 30 min, 25 °C) or with excess of p-tolylisocyanide at room temperature, cationic complexes $[\overline{\mathrm{Ru({=}C[Ph]OCH_2}}\mathrm{)(CO)_2(PPh_3)_2}]^+$, (**4**), and $[\overline{\mathrm{Ru({=}C[Ph]OCH_2}}\mathrm{)(CN}\text{-}p\text{-tolyl})_2(\mathrm{PPh_3})_2]^+$, (**5**), are formed and readily isolated as the perchlorate salts. Formation of the $[\overline{\mathrm{Ru{=}C[Ph]OCH_2}}]$ ring involves three processes: loss of halide from the metal, co-ordination of two molecules of π-acid, and the attack of the oxygen of the acyl ligand on the methylene centre. The presence of the strained four membered ring in (**5**) is confirmed by a *X*-ray diffraction study (Figure 2).‡ There is a significant difference in the carbon–oxygen bond lengths in the ring, with the shorter bond being to the carbene carbon. It should be noted that an alternative possible product, a benzyl derivative, from aryl migration onto methylene, is not seen in any of the above reactions.

Proposed mechanisms for the Fischer–Tropsch process, and the homogeneous catalytic hydrogenation of carbon monoxide, often suggest migration of the growing alkyl fragment to methylene intermediates. Given the diversity of likely intermediates in this chemistry [*i.e.* $-\mathrm{CHO}$, $\mathrm{CH_2O}$, $-\mathrm{CH_2OH}$, $=\mathrm{C(H)OH}$ fragments as ligands] the possible combination of methylene and acyl (or formyl) ligands, to form metallaoxetene intermediates of the type described above, deserves consideration. Perhaps such processes contribute to the 'oxygenate' fraction of the product in Fischer–Tropsch chemistry.

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