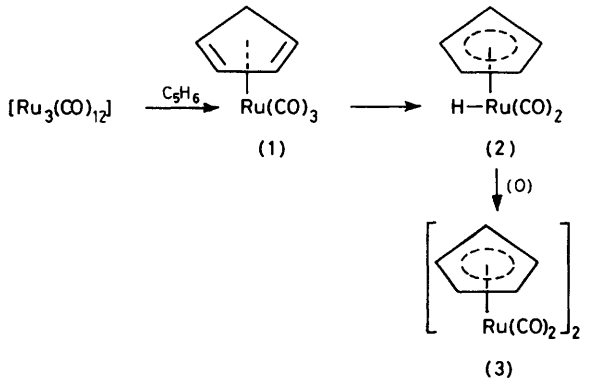
Formation of $[RuR(CO)_2(\eta^5\text{-}C_5H_5)]$ ($R = C_{10}H_{13}$ or $COC_{10}H_{13}$) † during the Reaction of $[Ru_3(CO)_{12}]$ with Cyclopentadiene

By **Amihai Eisenstadt, Felix Frolow,** and **Avi Efraty,*** Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel

The compound $[RuH(CO)_2(\eta^5\text{-}C_5H_5)]$ formed *in situ* during the reaction of $[Ru_3(CO)_{12}]$ with cyclopentadiene has been found to add in a stereo- and regio-specific manner to *endo*-dicyclopentadiene to afford the alkyl derivative $[Ru(C_{10}H_{13})(CO)_2(\eta^5\text{-}C_5H_5)]$ which undergoes a facile carbonylation to the acyl complex $[Ru(COC_{10}H_{13})(CO)_2(\eta^5\text{-}C_5H_5)]$. The structure of $[Ru(COC_{10}H_{13})(CO)_2(\eta^5\text{-}C_5H_5)]$ was determined by a single-crystal *X*-ray diffraction analysis; crystals are triclinic, space group $P\bar{1}$, $a = 6.342(1)$, $b = 7.144(2)$, $c = 81.491(4)$ Å, $\alpha = 86.65(3)$, $\beta = 85.98(4)$, $\gamma = 71.41(2)°$, and $Z = 2$. The final R value was 0.034 for 2402 observed reflections.

THE reaction of cyclopentadiene with $[Ru_3(CO)_{12}]$ was reported by Humphries and Knox [1] to proceed *via* (1) and (2) to the dimer (3). According to this procedure, (3) is produced in 60—70% yield by the oxidation of the hydrido-complex (2) which is formed relatively fast (1—2 h) in boiling heptane under an inert atmosphere. A similar reaction, carried out in methylcyclohexane



under reflux conditions, revealed a second major product, $[Ru(COC_{10}H_{13})(CO)_2(\eta^5\text{-}C_5H_5)]$ (5) (20—60%), together with small amounts (1—2%) of $[Ru(C_{10}H_{13})(CO)_2(\eta^5\text{-}C_5H_5)]$ (4) and ruthenocene. The origin and nature of these new complexes are described in this study.

RESULTS AND DISCUSSION

The white crystalline alkyl complex (4) and acyl complex (5) were characterized from their elemental composition data and spectroscopic properties. The i.r. spectra of (4) (2 010, 1 950 cm^{-1}) and (5) (2 022, 1 960, and 1 650 cm^{-1}) are consistent with the presence of two terminally bonded carbonyls in each complex as well as an acyl group in the latter. Fragmentations under electron-impact conditions (70 eV) ‡ of both complexes originate from the molecular ions [m/e(^{102}Ru) 356(4), 384(5)] and proceed *via* the normal decarbonylation steps and bond-breaking processes involving both intact and partially degraded ligands. In the ^{1}H n.m.r. spectra ($CDCl_3$) the cyclopentadienyl protons give rise to singlets [δ 5.20(4) and 5.29(5)], whereas resonances due to the $COC_{10}H_{13}$ and $C_{10}H_{13}$ moieties are rather complex.

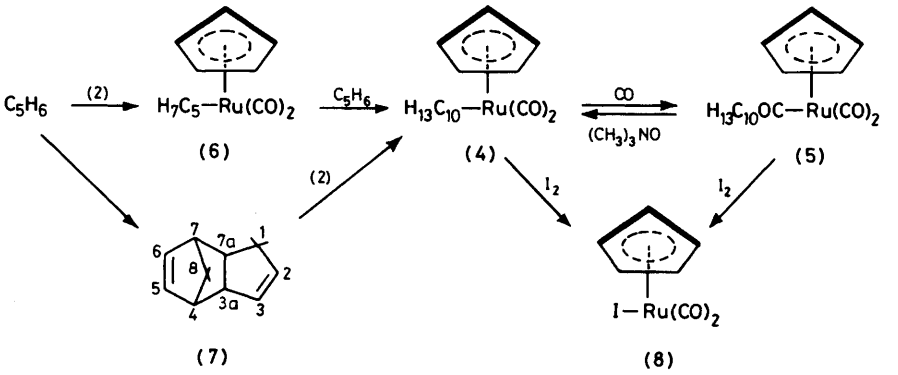
The origin of (4) may be traced to the addition of the '*in situ*' formed hydrido-complex (2) to either cyclopentadiene or dicyclopentadiene (see Scheme). Implication of cyclopentadiene requires a Diels–Alder [2 + 4] addition step to yield an intermediate of type (6). Since the carbonylation of (4) and (5) can only take place in the early stages of the process, it may be reasonable to assume that the formation and decay of the σ-alkyl complex (4) during this reaction is relatively fast. Attempts to improve the yield of (4) by changing the conditions during the course of this reaction invariably led only to trace amounts of the desired complex with the major products being (3) and (5). On the other hand, the formation of (4) by the decarbonylation of the acyl (5) may be accomplished in 37% yield on treatment with trimethylamine oxide.[2] This reaction most probably proceeds *via* the formation of the electronically and co-ordinatively unsaturated intermediate $[Ru(COC_{10}H_{13})(CO)(\eta^5\text{-}C_5H_5)]$ followed by its acyl to alkyl (4) rearrangement. Complex (4) is relatively stable in air and can be stored indefinitely when sealed under argon. Iodination of both (4) and (5) gave a quantitative yield of (8), identified by analogy with an authentic sample prepared by the iodination of (3).[3]

The ratio of the major products (3) and (5) obtained from reaction of $[Ru_3(CO)_{12}]$ with cyclopentadiene depends to a large extent on the concentrations of the reactants and the solvents. In solvents such as heptane and methylcyclohexane in the presence of a large molar excess (15—20) of cyclopentadiene, a concentrated $[Ru_3(CO)_{12}]$ reaction solution (*e.g.* 0.1—0.06 mmol cm^{-3}) was observed to effect higher yields complex (5) (50—60%) and lower yields of the dimer (3) (35—45%). Dilution of $[Ru_3(CO)_{12}]$ in the original reaction solution (*e.g.* 0.05—0.01 mmol cm^{-3}) effects a decrease in the yield of complex (5) (as low as 20%) and an increase in the yield of (3) (as high as 80%). Substituting the above cited solvents with boiling glyme (1,2-dimethoxyethane) led to the exclusive formation of (3) in a quantitative yield.

The stereochemical and mechanistic aspects of the

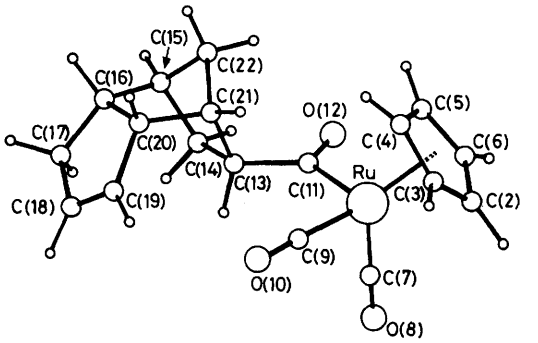
† Dicarbonyl(1—5-η-cyclopentadienyl)(tricyclo[5.2.1.0^{2,6}]dec-4-en-8-yl)ruthenium or dicarbonyl(1—5-η-cyclopentadienyl)(tricyclo[5.2.1.0^{2,6}]dec-4-en-8-ylcarbonyl)ruthenium.

‡ Throughout this Note: 1 eV ≈ 1.602×10^{-19} J; and 1 Torr = (101 325)/760 Pa.



SCHEME

reactions leading to the formation of (4) and (5) could not be resolved by simple spectroscopic techniques. The ^1H n.m.r. spectra of the $C_{10}H_{13}$ unit in both (4) and (5) consist of a multitude of resonances for which rigorous assignments were not possible. Since complex (5) was found to be sufficiently stable and yielded crystals suitable for a diffraction study, the structure of this complex was determined by a complete *X*-ray analysis.



The molecular geometry of $[Ru(COC_{10}H_{13})(CO)_2(\eta^5\text{-}C_5H_5)]$ (5)

The molecular geometry of (5) is illustrated in the Figure and some representative interatomic distances and bond angles are given in Table 1. The features of the $Ru(CO)_2(\eta^5\text{-}C_5H_5)$ unit are straightforward. In relationship to the average C_5H_5 plane, the acyl keto-atoms C(11) and O(12) are displaced by 2.949(3) and 2.588(3) Å, respectively. The tricyclic organic unit ($C_{10}H_{13}$) assumes an *endo* configuration, and the acyl is *exo* linked at the C(13) position. A double bond C(18)–C(19) [1.354(10) Å] found in the organic unit is significantly shorter than its nearest neighbours [C(17)–C(18) 1.428(11) and C(19)–C(20) 1.496(10) Å] which are of sp^2–sp^3 hybridization; whereas the remaining C–C bonds are of sp^3–sp^3 hybridization [average 1.538(16) Å].

Certain noteworthy conclusions may be reached concerning the formation of (4), assuming that its carbonylation to (5) takes place with retention of configuration at

TABLE 1

Bond lengths (Å) and angles (°) for $[Ru(COC_{10}H_{13})(CO)_2(\eta^5\text{-}C_5H_5)]$ (5)

C(7)–Ru(1)	1.862(7)	C(9)–Ru(1)	1.869(6)
C(11)–Ru(1)	2.090(6)	C(3)–C(2)	1.407(11)
C(4)–C(3)	1.412(11)	C(5)–C(4)	1.397(9)
C(6)–C(5)	1.403(10)	C(2)–C(6)	1.412(10)
O(8)–C(7)	1.156(8)	O(10)–C(9)	1.132(7)
O(12)–C(11)	1.211(7)	C(13)–C(11)	1.532(8)
C(14)–C(13)	1.544(7)	C(21)–C(13)	1.545(7)
C(15)–C(14)	1.514(10)	C(16)–C(15)	1.550(10)
C(22)–C(15)	1.521(10)	C(17)–C(16)	1.520(10)
C(20)–C(16)	1.546(9)	C(18)–C(17)	1.428(11)
C(19)–C(18)	1.354(10)	C(20)–C(19)	1.496(10)
C(21)–C(20)	1.549(9)	C(13)–C(21)	1.545(7)
C(22)–C(21)	1.562(9)	C(15)–C(22)	1.521(10)
O(8)–Ru(1)–C(7)	0.8(2)	C(9)–Ru(1)–C(7)	91.8(3)
O(10)–Ru(1)–C(9)	1.4(2)	C(11)–Ru(1)–C(7)	83.6(3)
C(11)–Ru(1)–O(10)	94.5(2)	C(6)–C(2)–C(3)	107.9(7)
C(4)–C(3)–C(2)	107.8(6)	C(5)–C(4)–C(3)	108.0(6)
C(6)–C(5)–C(4)	108.5(6)	C(5)–C(6)–C(2)	107.8(6)
O(8)–C(7)–Ru(1)	177.9(6)	O(10)–C(9)–Ru(1)	176.4(5)
O(12)–C(11)–Ru(1)	117.9(5)	C(13)–C(11)–Ru(1)	121.6(4)
C(13)–C(11)–O(12)	120.4(5)	C(14)–C(13)–C(11)	113.8(5)
C(21)–C(13)–C(11)	110.1(5)	C(21)–C(13)–C(14)	102.2(5)
C(15)–C(14)–C(13)	105.0(5)	C(16)–C(15)–C(14)	110.7(6)
C(22)–C(15)–C(14)	100.8(6)	C(22)–C(15)–C(16)	100.8(6)
C(17)–C(16)–C(15)	118.5(6)	C(20)–C(16)–C(15)	103.0(5)
C(20)–C(16)–C(17)	104.6(6)	C(18)–C(17)–C(16)	106.8(6)
C(19)–C(18)–C(17)	113.5(7)	C(20)–C(19)–C(18)	109.5(7)
C(19)–C(20)–C(16)	105.4(6)	C(21)–C(20)–C(16)	103.8(5)
C(21)–C(20)–C(19)	118.9(6)	C(20)–C(21)–C(13)	109.5(5)
C(22)–C(21)–C(13)	99.8(5)	C(22)–C(21)–C(20)	100.7(5)

TABLE 2

Atomic co-ordinates ($\times 10^4$) of $[Ru(COC_{10}H_{13})(CO)_2(\eta^5\text{-}C_5H_5)]$ (5) with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Ru(1)	2 862(1)	10 436(1)	1 370(1)
C(2)	3 038(10)	12 804(8)	516(3)
C(3)	4 872(10)	12 455(8)	949(4)
C(4)	4 040(9)	12 953(8)	1 665(4)
C(5)	1 716(9)	13 643(7)	1 667(3)
C(6)	1 079(9)	13 530(7)	964(3)
C(7)	1 665(10)	8 891(8)	854(3)
O(8)	904(10)	7 978(7)	517(3)
C(9)	5 248(8)	8 239(8)	1 636(3)
O(10)	6 759(7)	6 936(6)	1 767(3)
C(11)	742(7)	9 905(7)	2 218(3)
O(12)	−1 169(6)	10 981(7)	2 252(3)
C(13)	1 589(7)	8 282(7)	2 805(2)
C(14)	−283(9)	7 878(9)	3 306(3)
C(15)	130(10)	8 386(10)	4 055(3)
C(16)	2 239(10)	6 835(9)	4 350(3)
C(17)	2 512(12)	4 656(10)	4 292(4)
C(18)	4 305(12)	3 890(9)	3 768(4)
C(19)	5 313(10)	5 226(9)	3 516(4)
C(20)	4 142(9)	7 176(8)	3 845(3)
C(21)	2 934(8)	8 954(7)	3 344(2)
C(22)	993(11)	10 123(9)	3 872(3)

the C(13) site. This complex can only be derived by a stereo- and regio-specific *exo*-addition of the Ru–H bond in (2) to the C(5) position of the *endo* form of 3a,4,7,7a-tetrahydro-4,7-methanoindene [*endo*-dicyclopentadiene, (7)]. A two step process *via* (6) can be ruled out since this requires addition at either the C(2) or C(3) positions in (7). Although the preparation of several $[RuR(CO)_2(\eta^5\text{-}C_5H_5)]$ complexes, especially with fluorocarbons, by a different route has already been reported,[4,5] the formation of (4) through a highly specific hydride-addition reaction is quite unusual. The stereochemical aspects of these addition and carbonylation reactions should be of interest, since similar steps are known to take place in homogeneous catalytic processes.

EXPERIMENTAL

The compound $[Ru_3(CO)_{12}]$ was purchased from Strem Chemicals Inc. (U.S.A.). Cyclopentadiene was freshly prepared before use, and solvents were degassed and redistilled. An argon atmosphere was routinely provided for the following operations: (*i*) carrying out reactions, (*ii*) admitting to evacuated vessels, (*iii*) handling solutions of organometallic compounds, and (*iv*) storage of organometallic solids.

Microanalyses were performed by the microanalytical laboratory at the Weizmann Institute. I.r. spectra were recorded on a Perkin-Elmer 467 grating spectrometer and were calibrated with the aid of a polystyrene film; ^1H n.m.r. spectra were obtained at 90 MHz using a Bruker HFX-10 spectrometer, and mass spectra on a NAT-ATLAS CH-4 spectrometer.

Reaction of $[Ru_3(CO)_{12}]$ *with Cyclopentadiene.*—Freshly distilled cyclopentadiene (1.5 cm^3, 18.2 mmol) and $[Ru_3(CO)_{12}]$ (0.34 g, 0.52 mmol) were allowed to react in boiling methylcyclohexane (10 cm^3) for 5 h. The reaction mixture was cooled down to ambient temperature, the solvent removed under vacuum (40 °C, 20 Torr), and the dry mixture mixed with neutral alumina placed on top of an alumina column. The products were eluted in the following order: (4) (hexane), ruthenocene (hexane), (5) (hexane–acetone, 5 : 1 v/v), and (3) (hexane–acetone, 4 : 1 v/v). Characterization and/or identification of products were carried out: $[Ru(C_{10}H_{13})(CO)_2(\eta^5\text{-}C_5H_5)]$ (4), 0.01 g (1.8%), white, m.p. 68—79 °C (Found: C, 57.35; H, 5.10. Calc. for $C_{17}H_{18}O_2Ru$: C, 57.60; H, 5.15%), exact mass of the molecular ion m/e = 356.0368, i.r. (hexane) 2 010vs and 1 950vs cm^{-1}; ruthenocene, 0.003 g (1.3%), identified by comparison with an authentic sample;[6] $[Ru(COC_{10}H_{13})(CO)_2(\eta^5\text{-}C_5H_5)]$ (5), 0.195 g (32.5%), white, m.p. 110—112 °C (Found: C, 56.30; H, 4.70. Calc. for $C_{18}H_{18}O_3Ru$: C, 56.95; H, 4.95%), i.r. (hexane) 2 022vs, 1 960vs, and 1 650vs cm^{-1}; $[\{Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ (3), 0.231 g (66%), identified by comparison with an authentic sample.[7-9]

Conversion of $[Ru(COC_{10}H_{13})(CO)_2(\eta^5\text{-}C_5H_5)]$ (5) *into* $[Ru(C_{10}H_{13})(CO)_2(\eta^5\text{-}C_5H_5)]$ (4) *with* $(CH_3)_3NO$.—A solution of (5) (0.16 g, 0.416 mmol) in acetone (20 cm^3) was refluxed with anhydrous $(CH_3)_3NO$ (0.345 g, 4.6 mmol) for 14 h. The reaction mixture was cooled to ambient temperature, filtered, and the filtrate dried under vacuum (40 °C, 20 Torr). The product mixture was separated on a neutral alumina column and identified as already described, to give unreacted (5) (0.075 g) and (4) [0.030 g, 37% yield, calculated on the basis of the amount of (5) which entered into the reaction].

X-*Ray Diffraction Analysis of* $[Ru(COC_{10}H_{13})(CO)_2(\eta^5\text{-}C_5H_5)]$ (5).—Appropriate crystals of (5) were obtained by slow evaporation of a hexane solution of the complex. The structure was resolved from the *X*-ray diffraction analysis of $C_{18}H_{18}O_3Ru$ (5): M = 383.4, triclinic, space group $P\bar{1}$, a = 6.342(1), b = 7.144(2), c = 18.491(4) Å, α = 86.65(3), β = 85.98(4), γ = 71.41(2)°, U = 791.5 Å^3, D_m = 15.4, Z = 2, D_c = 1.55 g cm^{-3}, $F(000)$ = 367.99, $\mu(Mo\text{-}K_\alpha)$ = 9.50 cm^{-1}. Data were collected on a computer-controlled CAD-4 diffractometer [$\lambda(Mo\text{-}K_\alpha)$ = 0.7114 Å] at 20 °C. The structure was solved by the heavy-atom technique using 2 402 unique reflections with $F_o > 3\sigma(F_o)$. Full-matrix least-squares refinement of all atomic positions converged to a conventional R and weighted R' factors of 0.034 and 0.035, respectively [$w = 1.5484/\sigma^2(F_o) + 0.001(F_o)^2$].* All calculations were performed with the SHELX-76 [10] package of crystallographic programs. Final atomic co-ordinates are listed in Table 2. Hydrogen atom co-ordinates, anisotropic thermal parameters, and observed and calculated structure factors are available as Supplementary Publication No. SUP 23234 (18 pp.).†

This research program was supported by a grant received from the U.S.A.—ISRAEL Binational Science Foundation (BSF).

[1/1517 *Received*, 30*th September*, 1981]

* The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this Note.

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

REFERENCES

[1] A. P. Humphries and S. A. R. Knox, *J. Chem. Soc., Dalton Trans.*, 1975, 1710.
[2] J. A. Gladysz, J. C. Selover, and C. E. Strouse, *J. Am. Chem. Soc.*, 1978, **100**, 6766.
[3] R. J. Haines and A. L. Du Preez, *J. Chem. Soc., Dalton Trans.*, 1972, 944.
[4] T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. A*, 1968, 2158.
[5] J. A. S. Howell and A. J. Rowen, *J. Chem. Soc., Chem. Commun.*, 1979, 482.
[6] D. E. Bubliz, W. E. McEwen, and J. Kleinberg, *Org. Synth.*, 1973, **5**, 1001.
[7] E. O. Fischer and A. Volger, *Z. Naturforsch., Teil B*, 1962, **17**, 421.
[8] T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc. A*, 1968, 2158.
[9] A. P. Humphries and S. A. R. Knox, *J. Chem. Soc., Chem. Commun.*, 1973, 326.
[10] SHELX-76 system of computer programs, G. M. Sheldrick, University of Cambridge, 1976.