Notes

Crystal Structure of $[Ni_2Ru_3(\eta\text{-}C_5H_5)_2(CO)_9(\mu_5\text{-}PPh)]$,† an Open Square-pyramidal Cluster obtained *via* Condensation of Co-ordinatively Unsaturated $[Ru_3(\mu\text{-}H)(CO)_9(\mu\text{-}PPh_2)]$ with $[Ni_2(\eta\text{-}C_5H_5)_2(CO)_2]$

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The novel pentanuclear cluster $[Ni_2Ru_3(\eta\text{-}C_5H_5)_2(CO)_9(\mu_5\text{-}PPh)]$ (**2**) has been obtained *via* 'condensation' of $[Ni_2(\eta\text{-}C_5H_5)_2(CO)_2]$ with the 46-electron complex $[Ru_3H(CO)_9(\mu\text{-}PPh_2)]$ (**1**) and reductive elimination of benzene. Its structure has been determined by *X*-ray diffraction methods. Crystals are monoclinic, space group $P2_1/a$ with a = 21.122(6), b = 12.656(2), c = 21.149(8) Å, β = 99.53(2)°, and Z = 8. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least squares to R = 0.056 for 4 318 observed reflections. Two crystallographically independent, but almost identical, pentanuclear clusters are present in which the metals are in an open square-pyramidal arrangement with the phosphorus from the PPh ligand interacting with all of them.

The synthesis, structural chemistry, and reactivity patterns of polynuclear clusters incorporating transition metals and main-group elements in the skeletal framework are the focus of considerable current interest.[1] We are investigating new synthetic strategies to gain access to higher nuclearity metal–sulphur and –phosphorus systems. The co-condensation of bi- and poly-metallic fragments is a potentially useful route to such compounds and the mixed-metal sulphur clusters $[M_2Fe_2(\eta\text{-}C_5H_5)_2(CO)_6(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2]$ (M = Cr or Mo)[2,3] and $[Ni_2Fe(\eta\text{-}C_5H_5)_2(CO)_3(\mu_3\text{-}S)]$[4] have thus been obtained *via* reactions of $[Fe_2(CO)_6(\mu\text{-}S)_2]$ with $[\{M(\eta\text{-}C_5H_5)(CO)_2\}_2]$ and $[\{Ni(\eta\text{-}C_5H_5)(CO)\}_2]$. A spiked triangular phosphido-bridged compound, $[Ni_2Fe_2(\eta\text{-}C_5H_5)_2(CO)_5(\mu_4,\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)]$ is likewise the major product from $[Fe_2(CO)_6(\mu,\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)]$ and $[\{Ni(\eta\text{-}C_5H_5)(CO)\}_2]$.[5]

In this paper we describe a new approach to the synthesis of higher nuclearity mixed-metal phosphinidene clusters. This involves condensation of the electronically unsaturated 46-electron trinuclear cluster $[Ru_3(\mu\text{-}H)(CO)_9(\mu\text{-}PPh_2)]$ (**1**), which contains an activated P–Ph bond and readily eliminates benzene on pyrolysis,[6] with the binuclear complex $[\{Ni(\eta\text{-}C_5H_5)(CO)\}_2]$ to afford $[Ni_2Ru_3(\eta\text{-}C_5H_5)_2(CO)_9(\mu_5\text{-}PPh)]$ (**2**), an open square-pyramidal metal cluster. To our knowledge (**2**) is one of few pentametallic NiRu clusters in the literature, and the first example of such a molecule with an open square-pyramidal metal framework. An additional feature of interest is the presence of a weak 'through the core' interaction between the apical phosphinidene and a ruthenium atom.

Experimental

Preparation.—Treatment of complex (**1**) (75 mg, 0.1 mmol) with $[\{Ni(\eta\text{-}C_5H_5)(CO)\}_2]$ (65 mg, 0.2 mmol) in refluxing hexane under a dry nitrogen atmosphere for 40 min, followed by thin-layer chromatography [Kieselgel P. F. Merck; eluant diethyl ether–light petroleum (b.p. 40–70 °C)(1:10)] gave (**2**) (27%), unreacted nickel dimer (40%), and a small amount of still uncharacterized dark brown product. The spectroscopic and analytical data for (**2**) [ν_{CO}(hexane–$CHCl_3$) at 2 066s, 2 032s, and 2 012vs cm^{-1}; ^{1}H n.m.r. ($CDCl_3$), δ 7.42—7.19 (m, 5 H, Ph) and 5.57 (s, 10 H, C_5H_5); fast-atom bombardment mass spectrum, *m/z* = 660 (P^+)] indicate a high local symmetry for all terminal CO groups, the presence of two equivalent cyclopentadienyl groups, and a single phenyl group.

Crystallography.—*Crystal data.* $C_{25}H_{15}Ni_2O_9PRu_3$, M = 910.99, monoclinic, a = 21.122(6), b = 12.656(2), c = 21.149(8) Å, β = 99.53(2)°, U = 5 576(3) Å^3 (by least-squares refinement from the 2θ values of 30 accurately measured reflections, λ = 0.710 69 Å), space group $P2_1/a$, Z = 8, D_c = 2.170 g cm^{-3}, $F(000)$ = 3 520. A grey-green flattened crystal of approximate dimensions 0.15 × 0.28 × 0.28 mm was used, μ(Mo-K_α) = 30.00 cm^{-1}.

Data collection and processing. Siemens AED diffractometer, θ—2θ mode, niobium-filtered Mo-K_α radiation; 8 800 independent reflections measured ($3 \leqslant \theta \leqslant 24°$, $\pm h,k,l$), 4 318 being considered observed [$I \geqslant 2\sigma(I)$].

Structure analysis and refinement. Direct and Fourier methods, full-matrix least-squares refinement with Ru, Ni, and P atoms anisotropic in the last cycles; hydrogen atoms placed at their calculated positions in the final structure-factor calculations. Weighting scheme used in the last cycles: $w = 0.8432/[\sigma^2(F_o) + 0.002F_o]$, with $\sigma(F_o)$ from counting statistics. Final R and R' values were 0.056 and 0.068 respectively. Calculations were performed on the CYBER 76 computer

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† 1,1,1,4,4,4,5,5,5-Nonacarbonyl-2,3-bis(η-cyclopentadienyl)-μ_5-phenylphosphanetetrayl-*cyclo*-dinickeltriruthenium (4*Ni–Ru*, 3*Ru–Ru*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses for the non-hydrogen atoms of complex (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(11)	1 268(1)	1 128(1)	8 647(1)	C(111)	1 235(11)	1 151(18)	10 443(11)
Ru(21)	189(1)	2 410(1)	8 686(1)	C(121)	797(10)	1 894(18)	10 580(10)
Ru(31)	996(1)	2 774(1)	7 759(1)	C(131)	1 044(12)	2 890(20)	10 600(12)
Ru(12)	616(1)	2 590(1)	3 148(1)	C(141)	1 704(11)	2 722(19)	10 504(11)
Ru(22)	960(1)	3 953(1)	4 195(1)	C(151)	2 925(12)	2 319(19)	9 145(12)
Ru(32)	1 654(1)	4 001(1)	3 167(1)	C(161)	2 945(12)	1 828(20)	8 579(12)
Ni(11)	2 074(1)	2 674(2)	8 538(1)	C(171)	2 932(12)	2 676(22)	8 141(13)
Ni(21)	1 091(1)	2 232(2)	9 668(1)	C(181)	2 896(12)	3 609(20)	8 446(13)
Ni(12)	1 795(1)	1 990(2)	3 061(1)	C(191)	2 883(13)	3 423(22)	9 093(13)
Ni(22)	924(1)	1 923(2)	4 331(1)	C(201)	1 255(7)	4 643(12)	9 043(7)
P(11)	1 232(2)	3 214(4)	8 879(2)	C(211)	911(9)	5 033(14)	9 523(9)
P(12)	1 712(2)	2 651(4)	3 978(2)	C(221)	857(9)	6 133(15)	9 603(9)
O(11)	254(8)	−467(13)	8 790(8)	C(231)	1 173(10)	6 812(18)	9 252(10)
O(21)	1 523(8)	141(13)	7 420(8)	C(241)	1 538(9)	6 409(15)	8 824(9)
O(31)	2 263(9)	−225(15)	9 446(9)	C(251)	1 573(9)	5 354(15)	8 697(9)
O(41)	−489(7)	1 309(12)	9 631(7)	C(12)	312(9)	1 242(15)	2 895(9)
O(51)	−567(6)	4 389(11)	8 775(6)	C(22)	498(9)	3 171(15)	2 334(9)
O(61)	−781(7)	1 574(11)	7 588(7)	C(32)	−170(9)	2 987(15)	3 349(8)
O(71)	551(8)	4 977(15)	7 435(8)	C(42)	380(13)	3 698(20)	4 688(13)
O(81)	1 968(9)	2 776(15)	6 865(9)	C(52)	596(12)	5 185(23)	3 866(13)
O(91)	120(7)	1 740(12)	6 663(7)	C(62)	1 532(9)	4 610(16)	4 818(10)
O(12)	66(7)	466(12)	2 719(7)	C(72)	1 273(12)	5 237(22)	2 903(12)
O(22)	365(7)	3 467(12)	1 807(7)	C(82)	2 359(10)	4 737(16)	3 548(10)
O(32)	−680(7)	3 181(12)	3 436(7)	C(92)	1 957(11)	3 857(18)	2 421(11)
O(42)	−17(11)	3 666(17)	5 029(11)	C(102)	2 058(10)	1 432(17)	2 184(10)
O(52)	290(9)	5 947(16)	3 718(10)	C(112)	1 600(11)	772(19)	2 397(11)
O(62)	1 870(8)	5 027(13)	5 235(8)	C(122)	1 833(11)	347(17)	2 962(11)
O(72)	1 057(10)	6 070(17)	2 715(10)	C(132)	2 454(11)	715(19)	3 176(11)
O(82)	2 813(8)	5 159(14)	3 801(8)	C(142)	2 597(10)	1 404(17)	2 694(10)
O(92)	2 144(8)	3 865(13)	1 915(9)	C(152)	1 277(9)	501(15)	4 794(9)
C(11)	614(10)	201(18)	8 723(10)	C(162)	991(10)	1 134(16)	5 245(10)
C(21)	1 441(10)	597(17)	7 880(10)	C(172)	320(10)	1 287(16)	4 966(10)
C(31)	1 894(11)	333(19)	9 134(11)	C(182)	186(9)	779(16)	4 377(10)
C(41)	−203(10)	1 749(16)	9 290(10)	C(192)	759(10)	311(16)	4 277(10)
C(51)	−274(9)	3 632(14)	8 736(8)	C(202)	2 455(8)	2 587(13)	4 548(8)
C(61)	−403(10)	1 930(16)	7 999(10)	C(212)	3 038(9)	2 643(14)	4 328(8)
C(71)	726(11)	4 107(20)	7 539(11)	C(222)	3 600(10)	2 656(17)	4 793(10)
C(81)	1 624(12)	2 769(20)	7 247(12)	C(232)	3 583(9)	2 610(15)	5 428(9)
C(91)	437(10)	2 136(16)	7 115(10)	C(242)	3 029(10)	2 615(15)	5 644(9)
C(101)	1 786(12)	1 683(19)	10 375(11)	C(252)	2 428(9)	2 584(15)	5 215(9)

(Centro di Calcolo Elettronico dell'Italia Nord-Orientale, Bologna) using SHELX.[7] Atomic scattering factors, corrected for anomalous dispersion of Ru, Ni, and P, were taken from ref. 8. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 1.

Results and Discussion

The structure of complex (**2**) consists of two crystallographically independent but almost identical molecules, one of which is represented in the Figure together with the atom-numbering scheme. Selected bond distances and angles in the two molecules are given in Table 2.

Each molecule is characterized by a pentanuclear metal core of three Ru and two Ni atoms co-ordinated by nine terminal carbonyls (through the Ru atoms), by two cyclopentadienyl groups (through the Ni atoms), and by a PPh ligand interacting with all five metal atoms. The pentanuclear framework consists of three triangles with two edges of the central Ru_3 triangle bridged by Ni atoms. The structure can also be described as a double butterfly with dihedral angles between the central triangle Ru(1)Ru(2)Ru(3) and the triangles Ru(1)Ru(2)Ni(2) and Ru(1)Ru(2)Ni(1) of 121.7(1) [122.9(1)] and 121.4(1) [122.4(1)°] respectively (the former values refer to molecule 1 and the latter ones, in square brackets, to molecule 2). Alternatively the metal cluster can be described as an open square pyramid with two Ru and two Ni atoms at the vertices of the open base, the Ni(1) · · · Ni(2) distance of 3.461(3) [3.499(3) Å] precluding any bonding interaction between these atoms, with the third Ru atom occupying the apex. Within the Ru_3Ni_2 skeleton the metal–metal bonds have normal values {Ru–Ru 2.800(2)—2.840(3) [2.806(3)—2.823(3) Å] and Ru–Ni 2.583(3)—2.650(3) [2.577(3)—2.639(3) Å]}. To our knowledge complex (**2**) is the first example of an open square-pyramidal arrangement of three Ru and two Ni atoms. Only two pentametallic RuNi clusters have been reported, the 'wing-tip bridged butterfly' $[NiRu_4(CO)_9(\mu_4,\eta^2\text{-}C_2Pr^i)_2(\mu\text{-}PPh_2)_2]$[9] and the 'closed' square-pyramidal $[Ni_2Ru_3(\eta\text{-}C_5H_5)_2(CO)_6(\mu\text{-}CO)_2(\mu_4,\eta^2\text{-}C_2Ph_2)]$.[10] Homometallic open square-pyramidal clusters have been reported, $[Ru_5(CO)_{14}(\mu_5,\eta^2\text{-}C_2Ph)(\mu\text{-}PPh_2)]$ (**3**)[11] and $[Ru_5(CO)_{12}(\mu_5,\eta^2\text{-}C_2Ph)(\mu_3,\eta^2\text{-}PhC_2C_2Ph)(\mu\text{-}PPh_2)]$ (**4**),[12] both obtained by unfolding the closed square-pyramidal $[Ru_5(CO)_{13}(\mu_4,\eta^2\text{-}C_2Ph)(\mu\text{-}PPh_2)]$ (**5**).[11] In contrast, the metal skeleton of (**2**) is constructed from fragments of lower nuclearity.

An interesting feature of the structure of complex (**2**) is the bonding of the PPh ligand to the metal cluster: the phosphorus atom interacts with all five metal atoms, even if not equally strongly. The Ni–P and Ru–P bonds involving the basal metals are strong {Ni(1)–P 2.139(5) [2.146(5)], Ni(2)–P 2.141(5) [2.142(5)], Ru(2)–P 2.400(5) [2.385(5)], and Ru(3)–P 2.404(5) [2.410(5) Å]}; the Ru–P bond involving Ru(1) at the apex of the

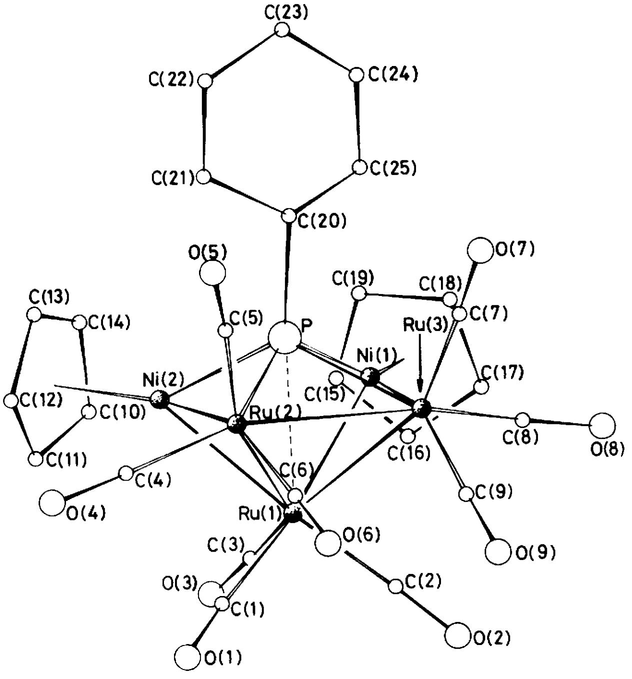


Figure. View of the one of the two crystallographically independent molecules of $[Ni_2Ru_3(\eta\text{-}C_5H_5)_2(CO)_9(\mu_5\text{-}PPh)]$ with the atomic numbering scheme

pyramid is weaker {Ru(1)–P 2.689(5) [2.665(4) Å]} but still significant.[6b] Two weak Ru–P bonds [2.496(2) and 2.632(2) Å] have been found in $[Ru_5(CO)_{16}(\mu\text{-}PPh_2)(\mu_5\text{-}P)]$ [6b] in which the phosphide atom interacts with all five Ru atoms of a very open metal arrangement containing only five metal–metal bonds. Other long M–P interactions have been found in $[Rh_9(CO)_{21}P]^{2-}$ [13] and $[Rh_{10}(CO)_{22}P]^{3-}$ [14] [up to 3.057(3) or to 3.015(14) Å respectively], but in these cases a 'naked phosphorus' is encapsulated inside the cavity of the metal cluster. In complex (**2**) the P atom from the PPh ligand is only 0.919(5) [0.907(5) Å] out of the perfectly planar open square base, whereas the Ru atom at the apex is 1.769(1) [1.758 (1) Å] distant on the opposite side. In $[Ru_5(CO)_{15}(\mu_4\text{-}PPh)]$,[15] where the phosphinidene ligand caps a closed square base of a pyramidal metal arrangement, the P and Ru atoms are above and below the basal plane (1.235 and 1.990 Å, mean values for the two independent molecules).

Also, μ_4-PR co-ordination of a phosphinidene to an open tetrametallic cluster is rare: two recent examples are $[RhRuCo_2(\eta\text{-}C_5H_5)(CO)_{10}(\mu_4\text{-}PPh)]$ [16] and $[Co_4(CO)_3\{(F_2P)_2NMe\}_4(\mu_4\text{-}PPh)_2]$.[17]

The open square-pyramidal arrangement allows an atom to interact with all five metals. In the closed square-pyramidal cluster (**5**) the acetylide ligand interacts with the basal metals; opening of the metal cluster along one basal edge in complexes (**3**) and (**4**) forces the α-carbon of the acetylide into closer proximity to the apical metal, such that it can interact with all five metals.[11,12]

The weak interaction of the P atom with the apical Ru atom in complex (**2**) does not seem to be required by electronic

Table 2. Selected bond distances (Å) and angles (°)

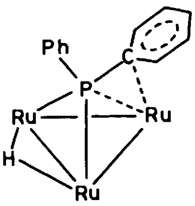
	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Ru(1)–Ru(2)	2.810(3)	2.806(3)	Ru(2)–C(4)	1.84(2)	1.76(3)
Ru(1)–Ru(3)	2.800(2)	2.823(3)	Ru(2)–C(5)	1.84(2)	1.82(3)
Ru(2)–Ru(3)	2.840(3)	2.817(3)	Ru(2)–C(6)	1.86(2)	1.83(2)
Ru(1)–Ni(1)	2.629(3)	2.639(3)	Ru(3)–C(7)	1.82(2)	1.80(3)
Ru(3)–Ni(1)	2.583(3)	2.577(3)	Ru(3)–C(8)	1.85(3)	1.83(2)
Ru(1)–Ni(2)	2.650(3)	2.619(3)	Ru(3)–C(9)	1.84(2)	1.81(2)
Ru(2)–Ni(2)	2.585(3)	2.588(3)	C(1)–O(1)	1.16(3)	1.14(2)
P–Ni(1)	2.139(5)	2.146(5)	C(2)–O(2)	1.17(3)	1.17(2)
P–Ni(2)	2.141(5)	2.142(5)	C(3)–O(3)	1.17(3)	1.15(2)
P–Ru(2)	2.400(5)	2.385(5)	C(4)–O(4)	1.16(3)	1.19(4)
P–Ru(3)	2.404(5)	2.410(5)	C(5)–O(5)	1.15(2)	1.17(3)
P–Ru(1)	2.689(5)	2.665(4)	C(6)–O(6)	1.17(2)	1.17(2)
P–C(20)	1.84(2)	1.82(2)	C(7)–O(7)	1.17(3)	1.19(3)
Ru(1)–C(1)	1.84(2)	1.87(2)	C(8)–O(8)	1.17(3)	1.15(3)
Ru(1)–C(2)	1.85(2)	1.85(2)	C(9)–O(9)	1.18(2)	1.20(3)
Ru(1)–C(3)	1.84(2)	1.85(2)			
Ni(1)–Ru(1)–Ni(2)	81.94(10)	83.44(12)	C(20)–P–Ru(3)	114.1(5)	116.2(6)
Ni(1)–Ru(1)–Ru(3)	56.72(9)	56.17(8)	C(20)–P–Ru(2)	116.3(5)	115.7(6)
Ru(3)–Ru(1)–Ru(2)	60.84(7)	60.06(8)	C(20)–P–Ni(2)	115.2(5)	112.7(6)
Ru(2)–Ru(1)–Ni(2)	56.43(9)	56.86(8)	Ru(1)–P–Ni(1)	64.8(2)	65.5(2)
Ni(2)–Ru(2)–Ru(1)	58.66(9)	57.92(9)	Ru(1)–P–Ni(2)	65.4(2)	65.0(2)
Ru(1)–Ru(2)–Ru(3)	59.41(7)	60.27(8)	Ru(1)–P–Ru(2)	66.8(1)	67.3(1)
Ru(2)–Ru(3)–Ru(1)	59.76(7)	59.68(8)	Ru(1)–P–Ru(3)	66.4(1)	67.4(1)
Ru(1)–Ru(3)–Ni(1)	58.29(8)	58.30(9)	Ru(1)–P–C(20)	176.9(5)	175.8(6)
Ru(3)–Ni(1)–Ru(1)	64.98(9)	65.52(8)	Ru(1)–C(1)–O(1)	172(2)	173(2)
Ru(2)–Ni(2)–Ru(1)	64.91(10)	65.23(8)	Ru(1)–C(2)–O(2)	171(2)	173(2)
Ni(1)–Ru(3)–Ru(2)	96.79(12)	97.37(11)	Ru(1)–C(3)–O(3)	176(2)	175(2)
Ru(3)–Ru(2)–Ni(2)	97.01(12)	97.81(11)	Ru(2)–C(4)–O(4)	174(2)	171(2)
Ni(1)–P–Ni(2)	107.9(2)	109.4(2)	Ru(2)–C(5)–O(5)	179(2)	169(2)
Ni(1)–P–Ru(3)	69.0(2)	68.6(2)	Ru(2)–C(6)–O(6)	176(2)	176(2)
Ru(3)–P–Ru(2)	72.5(2)	72.0(2)	Ru(3)–C(7)–O(7)	176(2)	176(2)
Ru(2)–P–Ni(2)	69.2(2)	69.5(2)	Ru(3)–C(8)–O(8)	173(2)	177(2)
C(20)–P–Ni(1)	112.3(5)	113.1(6)	Ru(3)–C(9)–O(9)	174(2)	174(2)

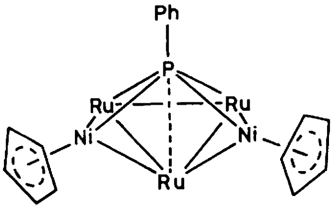
unsaturation of the metals, as all five obey the inert-gas rule. Counting the PPh ligand as a four-electron donor and the phosphorus as a part of the cluster framework, the polyhedral skeletal electron pair theory count[18] of 16 electrons or 8 skeletal pairs is appropriate for a *nido* pentagonal bipyramid. From the Figure the structure of complex (**2**) can be envisaged in this way, with a missing vertex lying in the equatorial plane, adjacent to the two Ni atoms, if the weak Ru–P bonding is neglected.

The synthesis of complex (**2**) from (**1**) under relatively mild reaction conditions follows the stoicheiometry (1) and can be

$$[\mathrm{Ru_3H(CO)_9(PPh_2)}] + [\mathrm{Ni_2}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{CO})_2] \longrightarrow [\mathrm{Ni_2Ru_3}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{CO})_9(\mathrm{PPh})] + 2\mathrm{CO} + \mathrm{C_6H_6} \quad (1)$$

said to result from the attack of a (η-C_5H_5)Ni unit on the unsaturated Ru atom of (**1**), followed by benzene elimination and by attack of a second (η-C_5H_5)Ni at the position vacated by the bridging hydride of (**1**). The presence of an excess of nickel fragments presumably prevents the formation of [$Ru_4(CO)_{13}(\mu_3$-PPh)].[6a] This proposed reaction path can readily be understood by comparing the structures of the precursor (**1**) and of the product (**2**).





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