Formation of [cyclic] [Ru[HN:C(Ph)OC:CHPh](CO)Cl[P(C6H4Me-p)3]2]. An anomalous insertion reaction of phenylacetylene with [Ru(CO)C1H(3,5-Me2Hpz)Ru(CO)C1H[P(C6H4Me-p)3]2] in ethanol/dichloromethane

A. Romero, A. Santos, and A. Vegas

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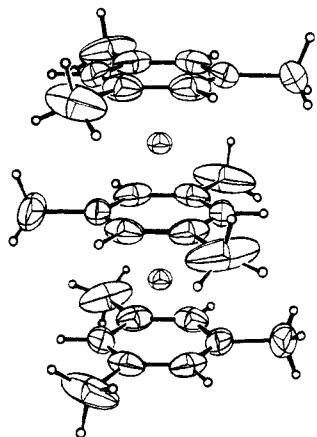- Copyright permission to reproduce figures and/or text from this article

Figure 1. ORTEP drawing (50% probability ellipsoids) of tris-(mesitylene)dichromium. C1 and C3 are the ring atoms, and C2 and C4 are the methyl C atoms in the central ring and terminal ring, respectively. The rings are as shown in the figure. The methyl groups on each ring could occupy either of two alternative sets of ring positions. For each ring the orientation has been chosen arbitrarily: the actual orientation of the methyl rings cannot be determined from the X-ray data. (See supplementary material for a discussion of the disorder.)

Table I. Selected Bond Distances (Å) and Angles (deg) for
$(\eta^6\text{-}C_6Me_3H_3)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6Me_3H_3)Cr_2$ (1)[a,b]

Bond Distances			
Cr–C1	2.190 (3)	C3–C3′	1.402 (2)
Cr–C3	2.131 (1)	C3–C3″	1.413 (2)
C1–C1′	1.417 (4)	C3–C4	1.517 (4)
C1–C2	1.510 (10)	Cr–Cr	3.338 (1)

Bond Angles			
C1′–C1–C1′	120	C3′–C3–C4	116.9 (4)
C1′–C1–C2	120	C3″–C3–C4	123.1 (4)
C3′–C3–C3″	120		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Since the central ring has $3m$ crystallographic symmetry, there is only one C–C ring distance and all of the C–C–C angles are 120°, whereas the terminal rings have $3m$ crystallographic symmetry so that there are two alternating independent C–C bond distances in the ring, and the two external C–C–C angles are not equal, even though all Cr–C distances are the same.

pentadienyl)$(\mu\text{-}\eta^5{:}\eta^5\text{-}$cyclopentadienyl)dinickel(1+)[5] triple-decker-sandwich compounds. As shown in Figure 1, all three mesitylene rings are planar, parallel, and nearly perfectly eclipsed when viewed down the threefold Cr–Cr axis which lies normal to the aromatic ring planes. Pertinent bond lengths and angles are given in Table I. The relative positions of methyl groups on adjacent rings cannot be determined due to the crystallographic disorder. (See supplementary material for further discussion.) The distance from Cr to the central ring plane is 1.669 (1) Å and to the terminal ring plane is 1.600 (1) Å. This should be compared with the Cr to ring distance of 1.609 (1) Å found in bis(benzene)chromium.[6] The elongated Cr bond to the bridging mesitylene ring in 1 accords well with the apparent susceptibility of this bond to thermolytic and oxidative cleavage.[1]

The Cr–Cr distance of 3.338 (1) Å in 1 is considerably longer than the average intermetallic spacing of 2.221 Å in the isoelectronic and structurally related tricarbonyl-bridged complex bis(η^6-benzene)tris(μ-carbonyl)dichromium[7] possessing a formal metal–metal triple bond.

The sum of the estimated single-bond covalent radii of Cr(0) is 2.96 Å,[8] suggesting that little or no direct interaction exists between the Cr centers in 1.[9] However, it is important to note that an elongated Cr–Cr bond of 3.281 (1) Å has been previously reported for the dimeric complex $[(\eta^5\text{-}C_5H_5)(CO)_3Cr]_2$.[8a]

The crystal structure confirms our earlier spectroscopic interpretations[1] and provides further support for the probable existence of higher nuclearity (arene)$_n$M$_{n-1}$ multiple-decker-sandwich oligomers and polymers.[10] We contend that such extended chain complexes most readily account for the stepwise formation of polynuclear arene-metal species in matrix-scale reactions of Cr, Mo, V, and Ti with arene substrates.[1,3] This is contrary to structural formulations originally proposed by Ozin and co-workers in which "arene- or polymer-stabilized metal clusters" consisting of two or more bound metal atoms sandwiched between a single pair of arene rings as in 3 ($n \geq 2$) were suggested.[3]

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(9) Metal–metal bonding through the center of the bridging ring in triple-decker-sandwich complexes has been suggested in at least one instance based on the comparatively short Mo–Mo distance (2.647 Å) and the 28-electron configuration in the complex $(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}P_6)Mo_2$ (cf. Scherer, O. J.; Sitzmann, H.; Wolmerhauser, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 351).

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Formation of
$[Ru\{HN{=}C(Ph)OC{=}CHPh\}(CO)Cl\{P(4\text{-}MeC_6H_4)_3\}_2]$. **An Anomalous Insertion Reaction of Phenylacetylene with** $[Ru(CO)ClH(3,5\text{-}Me_2Hpz)\{P(4\text{-}MeC_6H_4)_3\}_2]$ **in Ethanol/Dichloromethane**

A. Romero, A. Santos,* and A. Vegas

*Instituto de Quimica Inorganica "Elhuyar", CSIC
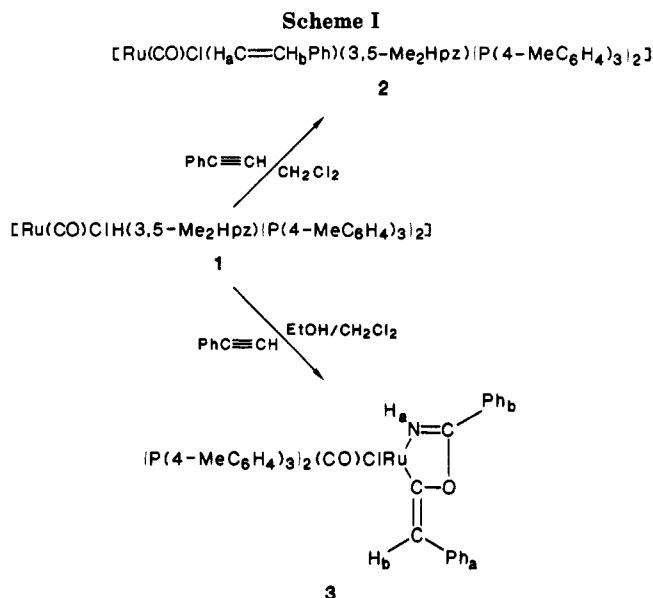Serrano, 113, 28006 Madrid, Spain*

Summary: An unusual reaction of $[Ru(CO)ClH(3,5\text{-}Me_2Hpz)\{P(p\text{-}MeC_6H_4)_3\}_2]$ with phenylacetylene in EtOH or EtOH/CH$_2$Cl$_2$ is described, in which a complex containing a new five-membered ruthenacycle, $[Ru\{NH{=}C(Ph)OC{=}CHPh\}(CO)Cl\{P(p\text{-}MeC_6H_4)_3\}_2]$, is formed, whose structure has been determined by X-ray crystallography. The reaction in CH$_2$Cl$_2$ yields the expected complex $[Ru(CO)Cl(HC{=}CHPh)(3,5\text{-}Me_2Hpz)\{P(p\text{-}MeC_6H_4)_3\}_2]$, resulting from insertion of phenylacetylene into the Ru–H bond.

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Scheme I

$[Ru(CO)Cl(H_aC\!=\!CH_bPh)(3,5\text{-}Me_2Hpz)\{P(4\text{-}MeC_6H_4)_3\}_2]$

2

PhC≡CH / CH₂Cl₂

$[Ru(CO)ClH(3,5\text{-}Me_2Hpz)\{P(4\text{-}MeC_6H_4)_3\}_2]$

1

PhC≡CH \ EtOH/CH₂Cl₂
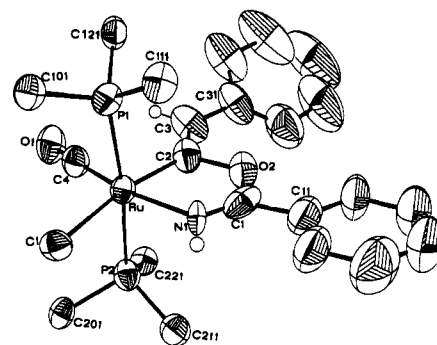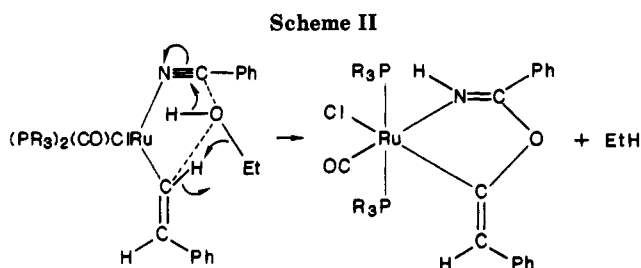
$\{P(4\text{-}MeC_6H_4)_3\}_2(CO)ClRu$

3

Figure 1. ORTEP drawing of **3**. Only the C atoms of the phosphine molecules directly bonded to the P atoms have been represented for clarity. Selected bond distances (Å) and angles (deg): Ru–P1 = 2.393 (4), Ru–P2 = 2.396 (4), Ru–Cl = 2.537 (4), Ru–N1 = 2.122 (8), Ru–C2 = 2.017 (14), Ru–C4 = 1.815 (15), N1–C1 = 1.18 (2), C1–O2 = 1.36 (2), O2–C2 = 1.49 (1), C1–C11 = 1.49 (2), C2–C3 = 1.30 (2), C3–C31 = 1.50 (2), C4–O1 = 1.11 (2), Ru–N1–C1 = 113.8 (9), N1–C1–O2 = 123 (1), C1–O2–C2 = 115 (1), O2–C2–C3 = 114 (1), C2–C3–C31 = 131 (1), N1–C1–C11 = 126 (1), O2–C1–C11 = 111 (1).

Scheme II

Insertion of acetylenes into transition-metal–hydrogen bonds is an important step in catalytic hydrogenation and considerable information about such reactions has become available in recent years.[1]   Phenylacetylene inserts into the Ru–H bond of [Ru(CO)ClH(PPh₃)₃] in two different ways, depending on the solvent, with formation of [Ru(CO)Cl(PPh₃)₂(HC=CHPh)] (in CH₂Cl₂) or [Ru(CO)Cl(PPh₃)₃(PhC=CH₂)] (in MeOH/CH₂Cl₂).[2]   Reactions of ruthenium hydride complexes containing P- and N-donor ligands with acetylenes have been to date not studied.   In this work we report our findings on the insertion reactions of phenylacetylene with [Ru(CO)ClH(3,5-Me₂Hpz){P(4-MeC₆H₄)₃}₂][3] (**1**).   The reactions studied are summarized in Scheme I.

Complex **2** is formed in good yield[4] in CH₂Cl₂ by the expected insertion reaction of the alkyne into the Ru–H bond, the insertion mode being cis.   However when the same reaction is carried out in CH₂Cl₂/EtOH or in EtOH, the unusual complex **3** is formed as the principal product.[5]   The IR spectrum showed clearly the presence of =NH and C=C bonds and the ¹H NMR spectrum revealed the presence of only one alkenylic proton.   The remaining

signals correspond to the iminic proton and to the protons of two phenyl and six p-MeC₆H₄ groups.   Attempts were made to assign to this complex a structure consistent with the analytical and spectral data.   The presence of two phenyl groups could correspond to a bis-insertion derivative of the alkyne, but the analytical data made it incompatible with the existence of a 3,5-dimethylpyrazole ligand in the complex.

The X-ray structure determination[6] of complex **3** revealed the formation of an unusual metallacycle which contains only one N atom from the 3,5-dimethylpyrazole ligand, one PhC= group from a phenylacetylene molecule, one phenylalkenyl fragment from one second phenylacetylene molecule, and one ether-like oxygen atom from ethanol.   A view of the molecule is represented in Figure 1.

The mechanism of formation of this metallacycle could imply, in a first step of reaction, a [2 + 2] attack of phenylacetylene on the N–N bond of the coordinated 3,5-dimethylpyrazole, as represented in eq 1.

The so-formed benzonitrile molecule, a second molecule of phenylacetylene (inserted previously into the Ru–H bond), and one ethanol molecule could originate the metallacycle in a second step as indicated in Scheme II.

Further studies on this and related unusual complexes are in progress to ascertain the generality of this reaction and to verify the mechanism proposed above.

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(4) Phenylacetylene (0.5 mL) was added to a solution of **1** in CH₂Cl₂ (87 mg, 0.1 mmol, 30 mL), and the mixture was refluxed for 2 h at room temperature. After concentration to 5 mL and addition of CH₂Cl₂ (5 mL) and petroleum ether (15 mL), a yellow solid precipitated in ca. 70% yield, which was washed with EtOH and petroleum ether. Recrystallization from CH₂Cl₂/petroleum ether gives analytically pure crystals of **2**. Anal. Calcd for C₅₈H₅₇ClN₂OP₂Ru: C, 69.16; H, 5.91; N, 2.88. Found: C, 69.04; H, 5.98; N, 2.75. IR (KBr disk): 3230 m, ν(NH); 1912 vs, ν(CO); 1568 m, ν(C=N); 1545 m, ν(C=C). ¹H NMR (360 MHz, CDCl₃, 20 °C, δ): 1.77, 1.92 (s, 3 H, Me), 2.29 (s, 18 H, 6Me), 5.43 (s, 1 H, CH), 5.73 (d, *J* = 16.7 Hz, 1 H, H_b), 6.74 (d, 2 H, Ph), 6.88 (t, 1 H, Ph), 6.97 (d, 8 H, C₆H₄), 7.02 (t, 2 H, Ph), 7.27 (d, 16 H, C₆H₄), 8.70 (d, *J* = 16.7 Hz, H_a), 11.07 (s, 1 H, HN) (standard SiMe₄).

(5) An excess of phenylacetylene (0.5 mL) was added to a suspension of **1** (52 mg, 0.06 mmol) in 30 mL of EtOH/CH₂Cl₂ (2:1), and the mixture was heated under stirring at 40 °C. After 2 h the red-orange solution was evaporated to dryness, and the solid was washed with diethyl ether several times (yield 40%). The red-orange solid was recrystallized from CH₂Cl₂/EtOH (1:1) to give crystals adequate for an X-ray structure determination. Anal. Calcd for C₅₈H₅₄ClNO₂P₂Ru: C, 69.98; H, 5.48; N, 1.41. Found: C, 69.85; H, 5.61; N, 1.39. IR (KBr disk): 3260 m, br, ν(NH); 1924 vs, ν(CO); 1580 m, ν(C=N); 1555 m, ν(C=C). ¹H NMR (360 MHz, CDCl₃, 20 °C, δ): 2.18 (s, 18 H, 6Me), 4.62 (s, 1 H, H_a), 6.70 (d, 2 H, Ph_a), 6.96 (m, 9 H, C₆H₄ + Ph_a), 7.00 (t, 2 H, Ph_a), 7.15 (d, 2 H, Ph_b), 7.19 (t, 1 H, Ph_b), 7.31 (t, 2 H, Ph_b), 7.53 (m, 16 H, C₆H₄) (standard SiMe₄).

(6) Crystal data for **3**, C₅₈H₅₄NP₂O₂ClRu, M_r 995.5: triclinic (P1̄), a = 13.134 (2) Å, b = 17.226 (1) Å, c = 13.070 (2) Å, α = 107.22 (1)°, β = 64.18 (1)°, γ = 102.36 (1)°, V = 2530.0 (6) Å³, Z = 2, D_calcd = 1.31 g cm⁻³, F(000) = 1032, μ(Cu Kα) = 39.8 cm⁻¹. A red-orange crystal (0.10 × 0.07 × 0.15 mm) was used to collect data on a Philips PW1100 diffractometer. A total of 6344 independent reflections were measured. Of them, 3884 with $I \geqslant 4\ \sigma(I)$ were considered as observed. The structure was solved by heavy-atom methods and refined with anisotropic parameters for all non-H atoms. A total of 586 parameters were varied by using unit weights. The final R = 0.064.
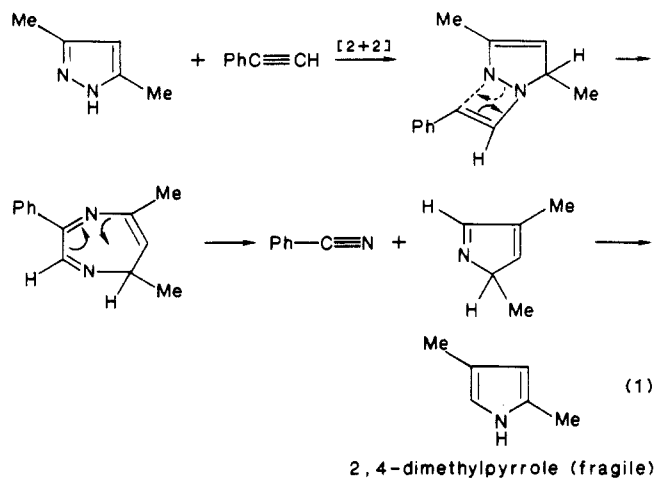
2,4-dimethylpyrrole (fragile)

Supplementary Material Available: Tables of final coordinates, thermal parameters, and bond distances and angles for **3** (6 pages), a table of observed and calculated structure factors for **3** (26 pages). Ordering information is given on any current masthead page.
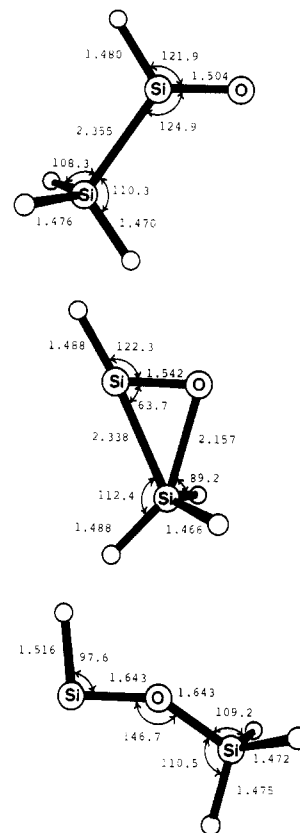

Figure 1. HF/6-31G* optimized geometries of **1**, **2**, and the transition state (middle) for the 1,2-silyl shift, in angstroms and degrees.

Table I. Barriers and Heats of Reaction (kcal/mol) for the 1,2-Silyl Shift in 1 to 2

level of theory[a]	barrier	heat of reactn
HF/6-31G*	30.7	−31.6
HF/6-31G**	30.7	−31.6
HF/6-31+G(2d,p)	29.4	−27.6
MP2/6-31G**	25.1	−19.6
MP3/6-31G**	26.1	−25.0
MP4SDTQ/6-31G**	24.5	−19.5
MP2/6-31+G(2d,p)	23.5	−17.5
MP3/6-31+G(2d,p)	24.3	−23.0
MP4SDTQ/6-31+G(2d,p)	22.9	−18.0
+ ZPC	22.7	−18.0

[a] For geometries, see Figure 1.

Theoretical Search for the Silanone-to-Silylene Isomerization

Takako Kudo and Shigeru Nagase*

Department of Chemistry, Faculty of Education
Yokohama National University, Yokohama 240, Japan

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Summary: In view of the current experimental interest in the title reaction, the barrier for the 1,2-shift in (H_3Si)-$HSi{=}O$ to $H\ddot{S}i{-}OSiH_3$ is investigated by means of ab initio calculations with flexible basis sets and electron correlation. It is found that the 1,2-silyl shift takes place under relatively mild conditions.

Silicon–oxygen doubly bonded compounds, silanones, are currently of growing interest.[1] In a series of papers,[2] we have calculated that the parent silanone is kinetically stable to isomerization as well as unimolecular destruction.[2a-c] It is of natural interest to investigate whether an appropriately substituted silanone would undergo isomerization.

Barton and co-workers[3-5] have continued to search for such experimental evidence and recently found that the copyrolysis of cyclotetrasiloxane and butadiene affords silacyclopentene.[4] They attempted to interpret this finding

in terms of the silylsilanone to siloxysilylene isomerization via a 1,2-silyl shift. However, an alternative mechanism has also been suggested[4] because a sizable barrier was calculated by us for the parent silanone.[2a-c] We report now the ab initio calculations of the 1,2-silyl shift in $(H_3Si)H$-$Si{=}O$ (**1**) to $H\ddot{S}i{-}OSiH_3$ (**2**).

In this report, all geometries were fully optimized at the Hartree–Fock (HF) level with the 6-31G* basis set[6] and identified as equilibrium or transition structures by calculating analytically the Hessian matrices. Energies were improved at the HF/6-31G* geometries with the larger basis sets and electron correlation. In the following, the symbol "//" means "at the geometry of".

In the isomerization of **1** to **2**, a relatively weak Si–Si bond is broken and a strong Si–O bond is formed. Reflecting this, the isomerization is ca. 18 kcal/mol exothermic (Table I), unlike the isomerization of the parent silanone which is approximately thermoneutral.[2a-c] In

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