Regioselective Nucleophilic Addition to Vinyl Carbenes (Metallabutadienes): Crystal Structure of [Ru{CH(CH=CPh$_2$)SC(NMe$_2$)S}(S$_2$CNMe$_2$)(CO)(PPh$_3$)]

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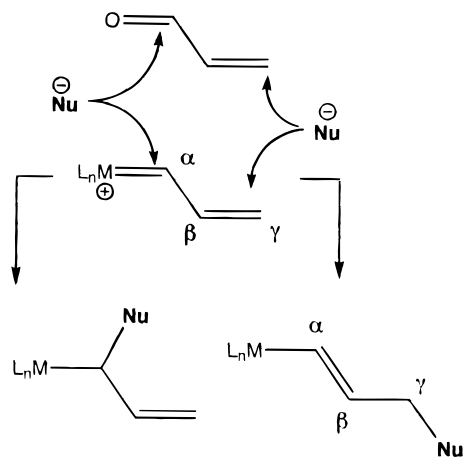
Summary: The new vinyl carbene salt [Ru(=C$_\alpha$HC$_\beta$H=C$_\gamma$Ph$_2$)(CO)(S$_2$CNMe$_2$)(PPh$_3$)$_2$]PF$_6$ (obtained from [RuHCl(CO)(PPh$_3$)$_3$], HC≡CCPh$_2$OH, Na[S$_2$CNMe$_2$], and HPF$_6$) reacts with fluoride, alkoxide, borohydride and hydroxide at C$_\gamma$ to give γ-functionalized σ-vinyl complexes, but with dithiocarbamate salts, attack occurs at C$_\alpha$ to provide the structurally characterized metallacycle [Ru{CH(CH=CPh$_2$)SC(NMe$_2$)S}(S$_2$CNMe$_2$)(CO)(PPh$_3$)].

With the advent of Grubbs' ROMP catalyst [Ru(=CHCH=CPh$_2$)Cl$_2$(PPh$_3$)$_2$],[1] interest has grown in the synthesis of vinyl carbene complexes[2] and in their applications to organic synthesis.[3] The Grubbs' approach involves the ring opening of diphenylcyclopropene, the synthesis of which is nontrivial;[4] however, more recently, the hydrometalation of propargylic alcohols has provided an alternative and more expedient approach, particularly appropriate for ruthenium.[2] If viewed as metallabutadienes, such complexes raise the question of the regioselectivity of attack by nucleophiles, the primary concern of this paper. Typically, alkylidene complexes of coordinatively saturated divalent ruthenium are prone to nucleophilic attack at the alkylidene carbon.[5] In the case of vinyl carbene complexes, however, attack at C$_\gamma$ (Scheme 1) is also plausible and reflects by microreversibility their synthesis via γ-dehydroxylation of γ-hydroxyvinyl ligands. Herein, we report (i) the synthesis of the salt [Ru(=CHCH=CPh$_2$)(CO)(S$_2$CNMe$_2$)(PPh$_3$)$_2$]PF$_6$; (ii) the reactions of this salt with a range of nucleophiles, all but one of which attack at C$_\gamma$; and (iii) the crystal structure of the metallacycle [Ru{CH(CH=CPh$_2$)SC(NMe$_2$)S}(S$_2$CNMe$_2$)(CO)(PPh$_3$)] which results from nucleophilic attack at C$_\alpha$ by dithiocarbamate salts.

Scheme 1



For this study, the new salt [Ru(=CHCH=CPh$_2$)(CO)(S$_2$CNMe$_2$)(PPh$_3$)$_2$]PF$_6$ (**1**) was chosen for the following reasons: (i) It is air and thermally stable and easily prepared on a large scale via the synthetic procedure outlined in Scheme 2; (ii) the co-ligand set is substitution-inert, precluding complications in mechanistic interpretation which might result from direct attack at the ruthenium center; (iii) the cationic charge on the complex is expected to activate the alkylidene toward nucleophilic attack. The synthesis from [RuHCl(CO)(PPh$_3$)$_3$] proceeds in high yield to provide deep red crystals of **1**, the formulation and stereochemistry of which rests firmly on spectroscopic data.[6] Most notable among these are the NMR data associated with the

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alkylidene ligand: The metallacumulene gives rise to three ^{13}C NMR resonances attributable to C_α (t, 311.8 ppm), C_β (148.2 ppm), and C_γ (161.4 ppm). The low-field region of the ^1H NMR spectrum features a double triplet at 14.72 ppm, showing discernible though not resolved coupling to two chemically equivalent phosphorus nuclei and H_β ($J(H_\alpha H_\beta) = 13.9$ Hz). The gross composition is confirmed by the appearance of a well-resolved isotopic distribution consistent with the complex molecular ion.

The reactions of **1** with a range of nucleophiles were investigated: Initially, the reaction with hydroxide ([*n*Bu$_4$N]OH) was investigated and shown to regenerate the precursor complex [Ru(CH=CHCPh$_2$OH)(CO)(S$_2$CNMe$_2$)(PPh$_3$)$_2$] (**2**)[6] in high yield (spectroscopically quantitative by $^{31}P\{^1H\}$ NMR), clearly resulting from nucleophilic attack at C_γ. In a similar manner, the reaction **1** with sodium ethoxide provided [Ru(CH=CHCPh$_2$OEt)(CO)(S$_2$CNMe$_2$)(PPh$_3$)$_2$] (**3**).[6] The alkoxide group is readily cleaved by HPF_6 to regenerate **1**. Treating **1** with [Bu$_4$N]F in thf provided the γ-fluorovinyl complex [Ru(CH=CHCPh$_2$F)(CO)(S$_2$CNMe$_2$)(PPh$_3$)$_2$] (**4**).[6] This complex is readily converted to **3** or **2** upon treatment with ethanol or water. The activation of C−F bonds of metal-bound trifluoromethyl groups is a notable feature of organoruthenium chemistry which has been extensively exploited by Roper;[7] however, the activation of a remote C−F bond as in the present case is, we believe, unprecedented. The reaction of **1** with ethanolic $NaBH_4$ provides exclusively the vinyl complex [Ru(CH=CHCHPh$_2$)(CO)(S$_2$CNMe$_2$)(PPh$_3$)$_2$] (**5**),[6] once again arising from attack at C_γ. No major tractable organometallic products have, however, been identified from the reactions of **1** with carbon nucleophiles including [Bu$_4$N]CN, LiPh, LiMe, LiC≡CPh, and BrMgC$_6$H$_4$-Me-4.

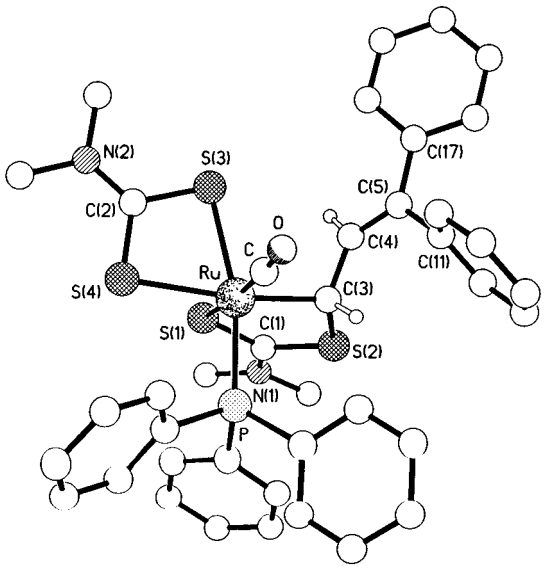

Figure 1. Geometry of **6t**. Phenyl hydrogen atoms have been omitted.

The reactions of **1** with a range of thiols and thiolates were investigated but failed to provide definitive results. In the case of sodium dimethyldithiocarbamate, however, a clean reaction ensued to initially provide the kinetic isomer (**6k**) which, however, slowly converted to the thermodynamic isomer (**6t**) of the metallacycle [Ru{CH(CH=CPh$_2$)SC(NMe$_2$)S}(S$_2$CNMe$_2$)(CO)(PPh$_3$)] (**6**). The thermodynamic isomer (**6t**) was characterized by a crystallographic study (Figure 1).[8] The geometry at ruthenium is distorted octahedral, with cis angles at ruthenium in the range 71.8(1)−98.8(1)°, the smaller value being associated with the bite of the dithiocarbamate ligand, which despite a normal pattern of delocalization (C(2)−S(3) 1.729(5) Å, C(2)−S(4) 1.715(5) Å) is noticeably asymmetrically bound to the ruthenium center (Ru−S(3) 2.486(1) Å, Ru−S(4) 2.453(1) Å). The larger of these is trans to the phosphine, whereas the shorter is trans to C(3), which might have been expected to show a pronounced trans influence. The Ru−S(1) separation at 2.434(1) Å is the shortest, consistent with it being trans to CO, the strongest π-acceptor ligand present. The C−S distances in the dithiocarbamatoalkylmetallacycle are distinctly asymmetric, in agreement with the valence bond description shown in Scheme 2. The Ru−C(3) bond at 2.148(5) Å is typical for alkyls of ruthenium(II). The chelate ring is clearly nonplanar, being folded out of plane by 25° about the C(3)−S(1) vector. While C(3)−C(4) is typical of a C(sp^2)−C(sp^2) single bond (being 1.492(7) Å), the

(6) Selected data for new complexes (satisfactory microanalytical data obtained; IR (Nujol, 25 °C), NMR (CDCl$_3$, 25 °C), FAB-MS (nba); Cumulene designation: Ru−C_α−C_β−C_γ; with the exception of **1** which was prepared on a 3 g scale, yields are based on 0.2 mmol scales). **1**: Yield 71%. IR: 1956 (ν(CO)), 1712, 1590 (C=CC=Ru) cm^{-1}. ^1H NMR: δ 2.34, 2.48 (s × 2, 6 H, NMe$_2$), 6.19 (d, 2 H, H^{2,6}(CC$_6$H$_5$), J(HH) = 8.0 Hz), 7.06 (d, 2 H, H^{2,6}(CC$_6$H$_5$), J(HH) = 6.9 Hz), 7.21−7.66 (m × 3, 36 H, C$_6$H$_5$), 8.06 (d, 1 H, H$_\beta$, $J(H_\alpha H_\beta)$ = 13.9 Hz), 14.72 (d, 1 H, $J(H_\alpha H_\beta)$ = 13.9 Hz, J(PH) not resolved) ppm. $^{13}C\{^1H\}$ NMR (CD$_2$Cl$_2$): 311.8 (Ru=C), 203.2 (t, RuCO, J(PC) = 13.4 Hz), 161.4 (C_γ), 148.2 (C_β), 141.7−130.0 (C$_6$H$_5$), 40.5 (NCH$_3$) ppm. $^{31}P\{^1H\}$ NMR: δ 33.9 ppm. FAB-MS: m/z 966 [M]$^+$, 774 [M − C$_3$H$_2$Ph$_2$]$^+$, 704 [M − PPh$_3$]$^+$. **2**: Yield spectroscopically quantitative (^{31}P NMR). IR: 3562 (νOH), 1907 (ν(CO)) cm^{-1}. ^1H NMR: δ 2.25, 2.53 (s × 2, 6 H, NMe$_2$), 5.44 (dt, 1 H, $J(H_\alpha H_\beta)$ = 16.9 Hz, J(PH$_\beta$) not resolved), 6.78 (m, 4 H, H^{2,6}(CC$_6$H$_5$)) 6.93 (dt, 1 H, H$_\alpha$, $J(H_\alpha H_\beta)$ = 16.8 Hz), 6.07 (m, 6 H, H$^{3-5}$(CC$_6$H$_5$)), 6.24 (m, 18 H, H$^{3-5}$(PC$_6$H$_5$)), 6.49 (m, 12 H, H^{2,6}(PC$_6$H$_5$)) ppm. $^{31}P\{^1H\}$ NMR: δ 41.0 ppm. FAB-MS: m/z 983 [M]$^+$, 966 [M − OH]$^+$, 774 [M − vinyl]$^+$, 704 [M − OH − PPh$_3$]$^+$. **3**: Yield 99%. IR: 1909 (ν(CO)) cm^{-1}. ^1H NMR: δ 1.04 (t, 3 H, CH$_2$C*H*$_3$, J(HH) = 6.6), 2.19, 2.52 (s × 2, 3 H × 2, NCH$_3$), 2.81 (q, 2 H, OCH$_2$, J(HH) = 6.6), 5.30 (d, 1 H, H$_\beta$, $J(H_\beta H_\alpha)$ = 13.2 Hz), 6.73, 7.05, 7.27, 7.51 (m × 4, 40 H, C$_6$H$_5$). $^{13}C\{^1H\}$ NMR: 206.4 (t, RuCO, J(PC) = 16.1), 206.1 (CS$_2$), 146.7 (t, C_α), 146.6−125.4 (C$_6$H$_5$ + C_β), 85.7 (C_γ), 58.0 (OCH$_2$), 38.5, 37.8 (NCH$_3$), 15.7 (C*C*H$_3$) ppm. $^{31}P\{^1H\}$ NMR: 41.64 ppm. FAB-MS: m/z 1011 [M]$^+$. **4**: Yield 91%. IR: 1905 (ν(CO)), 1144m (ν(CF)) cm^{-1}. FAB-MS: m/z 985 (1, [M]$^+$), 966 (8, [M − F]$^+$). The complex was insufficiently soluble for NMR analysis. **5**: Yield 97%. IR: 1905vs, 1893sh (ν(CO)) cm^{-1}. ^1H NMR: δ 2.21, 2.60 (s × 2, 3 H × 2, NCH$_3$), 4.13 (d, 1 H, H$_\gamma$, $J(H_\gamma H_\beta)$ = 7.3 Hz), 4.98 (dd, 1 H, H$_\beta$, $J(H_\gamma H_\beta)$ = 7.3, $J(H_\beta H_\alpha)$ = 15.6), 6.67 (dt, 1 H, H$_\alpha$, $J(H_\beta H_\alpha)$ = 15.6 Hz, J(PH$_\alpha$) not resolved), 6.55, 7.04, 7.22, 7.51 (m × 4, 40 H, C$_6$H$_5$). $^{31}P\{^1H\}$ NMR: 40.77 ppm. FAB-MS: m/z 967 [M]$^+$. **6t**: Yield 86%. IR: 1928 (ν(CO)) cm^{-1}. ^1H NMR: δ 3.11 (3 H), 3.29 (6 H), 3.36 (3 H) (s × 3, 12 H, NCH$_3$), 4.36 (dd, 1 H, H$_\alpha$, $J(H_\alpha H_\beta)$ = 12.3, J(PH$_\alpha$) = 5.4), 6.55 (d, 1 H, H$_\beta$, $J(H_\alpha H_\beta)$ = 12.3 Hz), 7.10, 7.20, 7.36 (m × 3, 25 H, C$_6$H$_5$). $^{13}C\{^1H\}$ NMR: 213.6 (d, S$_2$C, J(PC) = 1.9 Hz), 209.5 (s, S$_2$C), 201.5 (d, RuCO, J(PC) = 14.0), 143.7 (C^1(CC$_6$H$_5$)), 141.9 (C_β), 141.1−125.8 (C$_6$H$_5$), 129.5 (C_γ), 46.9, 44.2, 39.5, 39.3 (NCH$_3$), 35.1 (d, C_α, J(PC) = 6.5 Hz) ppm. $^{31}P\{^1H\}$ NMR: 53.2 ppm. FAB-MS: m/z 824 [M]$^+$, 796 [M − CO]$^+$, 736 [M − SCNMe$_2$]$^+$, 704 [M − S$_2$CNMe$_2$]$^+$.

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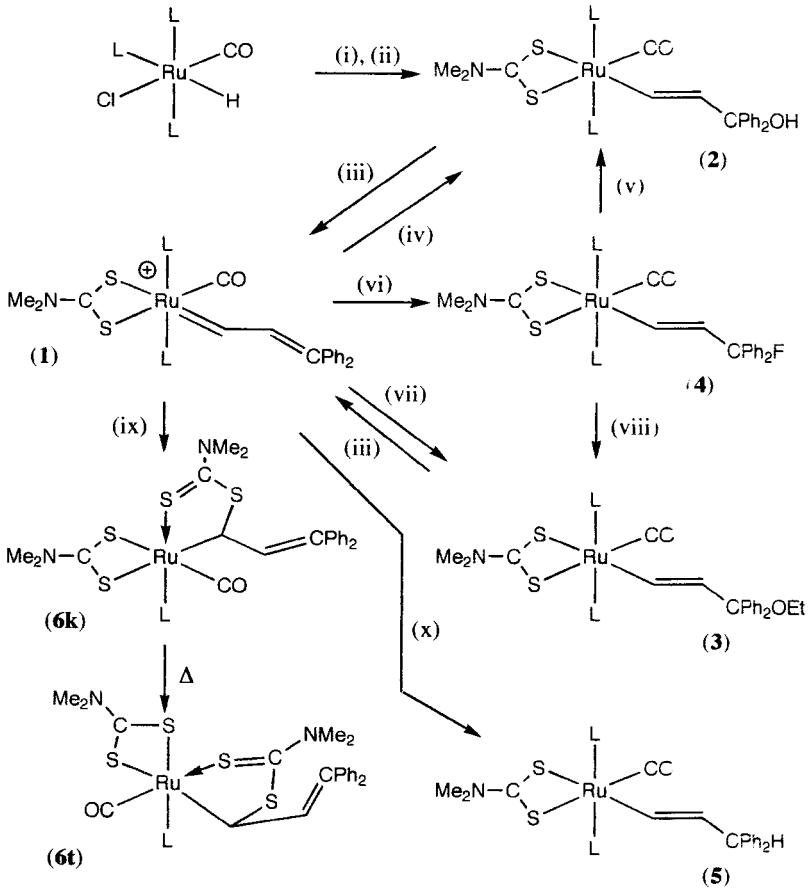
(8) Crystal data for **6t**: C$_{40}$H$_{39}$N$_2$OPRuS$_4$·2CHCl$_3$, M = 1062.8, monoclinic, space group *C*2/*c* (No.15), a = 18.627(2) Å, b = 19.801(2) Å, c = 25.717(4) Å, β = 95.34(1)°, U = 9444(2) Å^3, Z = 8, D_c = 1.495 g cm^{-3}, μ(Mo Kα) = 9.17 cm^{-1}, F(000) = 4320. An orange prism of dimensions 0.67 × 0.40 × 0.30 mm was used. Independent reflections (8280) were measured on a Siemens P4/PC diffractometer (graphite-monochromated Mo Kα radiation) using ω-scans. The structure was solved by direct methods, and all of the non-hydrogen atoms were refined anisotropically using full-matrix least squares based on F^2 and absorption-corrected data to give R_1 = 0.053 and wR_2 = 0.106 for 5810 observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 50°$] and 477 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Scheme 2[a]



[a] Reagents and conditions (25 °C unless otherwise stated): (i) $HC{\equiv}CCPh_2OH$ (CH_2Cl_2, 30 min); (ii) $Na[S_2CNMe_2]$ (CH_2Cl_2/EtOH, 15 min); (iii) HPF_6 (Et_2O, 30 min); (iv) $[Bu_4N]OH$ (CH_2Cl_2, 15 min); (v) H_2O (thf, 30m); (vi) $[Bu_4N]F$ (CH_2Cl_2, 1 h); (vii) NaOEt (CH_2Cl_2/EtOH, 30 min); (viii) EtOH (30 min); (ix) $Na[S_2CNMe_2]$ ($CHCl_3$, reflux, 12 h); (x) $NaBH_4$ (CH_2Cl_2/EtOH, 30 min).

C(4)−C(5) "double" bond is long at 1.347(7) Å, despite the absence of any apparent conjugation with the phenyl rings which, are rotated out of the plane of the double bond and its immediate substituents by 30° and 71°, respectively, for the rings based on C(17) and C(11).

The results discussed above indicate a general though not exclusive preference for nucleophilic attack to occur γ to the ruthenium in the present system. It might be argued that the steric bulk of the $Ru(S_2CNMe_2)(CO)(PPh_3)_2$ auxiliary predisposes the complex to attack remote from the metal; however, it should be noted that dithiocarbamate salts were the largest nucleophiles employed and these were nevertheless capable of attack at C_α. The possibility that the complex (**6t**) arises from coupling of the precoordinated dithiocarbamate and alkylidene ligands may be discounted since reaction of **1** with $[NH_4][S_2CN(CH_2)_4]$ provides the analogue of **6t** wherein the pyrollidinyl group resides exclusively on the metallacycle. The regioselectivity of attack at metallacumulenes is perhaps reminiscent of the more familiar 1,2 vs 1,4 regioselectivity encountered for α,β-unsaturated ketones (Scheme 1). Clearly, such regioselectivity will also be a function of the nature of the metallabutadiene in question, and we are extending our studies accordingly to address this question.

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Supporting Information Available: Tables of final atomic positional parameters and isotropic thermal parameters and an ORTEP representation for the structural analysis (9 pages). Ordering information is given on any current masthead page.

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