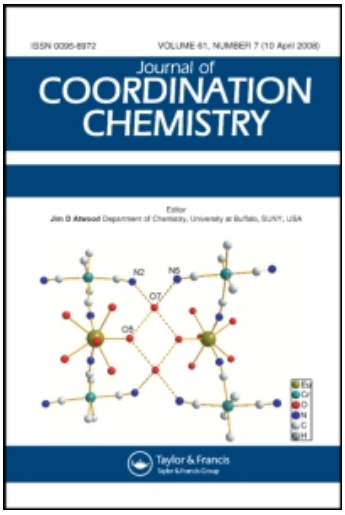

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Marcelo P. Gil[a]; Jairton Dupont[a]; Osvaldo L. Casagrande Jr.[a]
[a] Laboratory of Molecular Catalysis, Instituto de Química, UFRGS, Av. Bento, Porto Alegre, RS, Brazil

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HYDRORUTHENATION OF PROPARGYL AMINES PROMOTED BY THE 16-ELECTRON COMPLEX RuHCl(CO)(P*i*Pr$_3$)$_2$

MARCELO P. GIL, JAIRTON DUPONT and
OSVALDO L. CASAGRANDE JR.*

Laboratory of Molecular Catalysis, Instituto de Química, UFRGS, Av. Bento Gonçalves, 9500, Porto Alegre, RS, 91509-900, Brazil

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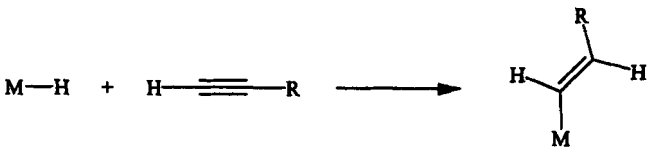
The 16-electron complex RuHCl(CO)(P*i*Pr$_3$)$_2$ (**1**) reacts with propargyl amines H–C≡C(CH$_2$)$_n$Y (**2–5**) ($n=1,2$; Y = NMe$_2$, N(Me)CH$_2$Ph, or Py) by insertion to afford the five-coordinate vinyl-complexes RuCl{(*E*)–CH=CH(CH$_2$)$_n$Y}(CO)(P*i*Pr$_3$)$_2$ (**6**, Y = NMe$_2$, $n=1$; **7**, Y = N(Me)CH$_2$Ph, $n=1$; **8**, Y = Py, $n=2$; **9**, Y = NMe$_2$, $n=2$) in good yield. Addition of CO to **7** produces the six-coordinate vinyl-complex RuCl{(*E*)–CH=CH(CH$_2$)$_n$Y}(CO)$_2$(P*i*Pr$_3$)$_2$ (**10**). The *trans* stereochemistry at the C=C bond is observed in all compounds. All compounds were characterized by IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy.

Keywords: Hydroruthenation; propargyl amines; vinyl compounds

INTRODUCTION

A typical reaction of transition-metal hydrides is the insertion of olefins and alkynes into the metal–hydride bond. This insertion process is, in general, kinetically highly favored yielding vinyl derivatives with *E* configuration (Equation 1).[1]



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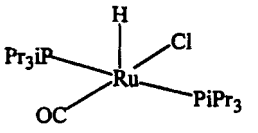
* Corresponding author. Tel.: 5551 316 6322. Fax: 5551 319 1499. E-mail: osvaldo@if.ufrgs.br.



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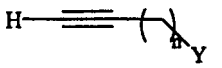


2, Y = NMe_2, n = 1
3, Y = $N(Me)CH_2Ph$, n = 1
4, Y = NMe_2, n = 2
5, Y = Py, n = 2

FIGURE 1 Ruthenium complex and propargyl amines used.

The insertion reactions and reactivity of terminal alkynes using Ru(II) and Os(II) have been investigated by Esteruelas and co-workers; their studies reveal that numerous organometallic compounds (vinyl,[2] hydrido dihydrogen alkynyl,[3] hydrido carbyne, hydrido vinylcarbyne,[4] and hydrido vinylidene[5] derivatives) can be obtained if the number of the hydrido ligands and the electronic properties of the starting complexes are appropriately selected. The choice of the R group of the alkyne also determines the nature of the obtained organometallic complexes. Thus, monohydrido species $MHCl(CO)(P\textit{i}Pr_3)_2$ (M = Ru, Os) reacts with acetylene, propyne, and phenylacetylene by insertion to give the five-coordinate vinyl-metal compounds $MCl\{(\textit{E})-CH=CHR\}(CO)(P\textit{i}Pr_3)_2$ (M = Ru, Os; R = H, Me, Ph).[2b] Reaction of $OsHCl(CO)(P\textit{i}Pr_3)_2$ with $HC{\equiv}CC(OH)R^1R^2$ affords, in one step, a vinylcarbene, $OsCl_2(=CHCH=CR^1R^2)(CO)(P\textit{i}Pr_3)_2$.[6]

We have recently studied the reactivity of propargyl amines and thioethers[7] to develop a new class of vinyl metal compounds *via* chlorometallation of the C–C triple bond by Pd and Pt compounds. This reaction failed however, with Ru compounds. We anticipated that such complexes could be prepared by hydroruthenation of propargyl amines using a 16-electron ruthenium compound (Figure 1).

EXPERIMENTAL

General Procedures

All manipulations were performed using vacuum-line or Schlenk techniques under a purified atmosphere. Solvents were stored under argon or vacuum prior to use. Toluene, hexane, and methyl-*tert*-butyl ether were distilled from Na/benzophenone ketyl and CH_2Cl_2 was distilled from P_2O_5. $RuHCl(CO)(P\textit{i}Pr_3)_2$ (1) was prepared following literature procedure.[8] 1-dimethylamino-2-propyne (2) and N-methyl-N-propargylbenzylamine (3) were

purchased from Aldrich and used as received. ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded with a Varian-300 spectrometer and calibrated against internal Me_4Si (^{1}H), internal $CDCl_3$ (^{13}C), or external H_3PO_4 (^{31}P) references. Coupling constants are reported in Hertz. Infrared spectra were recorded on a Bomem Michelson MB-102 FTIR spectrophotometer using KBr pellets or NaCl films. Elemental analyses were performed by the Central Analítica IQ/UFRGS (Porto Alegre, Brazil).

Synthesis of H–C≡CCH$_2$CH$_2$NMe$_2$ (4)

A solution of 3-butyn-1-ol (7.60 mL, 100 mmol) and NEt_3 (16.7 mL, 120 mmol) in CH_2Cl_2 (200 mL) was cooled to −50°C and methanesulfonyl chloride (9.30 mL, 77 mmol) was added dropwise affording a white suspension which was stirred for 20 min at −20°C. Water (60 mL) was added and the organic phase was extracted and dried with $MgSO_4$ overnight. The organic solution was filtered and the filtrate evaporated to yield H–C≡CCH$_2$CH$_2$SO$_2$Me as a yellow oil (13.30 g, 90%). To an excess anhydrous $HNMe_2$ (15.00 mL, 215.2 mmol) at −50°C, HC≡CCH$_2$CH$_2$SO$_2$Me (13.30 g, 89.8 mmol) was added and the resulting slurry was stirred for 24 h at room temperature. An aqueous KOH solution was added to the reaction mixture followed by addition of CH_2Cl_2 (60 mL). The organic phase was separated and treated with $MgSO_4$ overnight. The solution was filtered and the solvent removed under vacuum to afford a colorless oil. Yield (5.80 g, 68%). IR (KBr, cm^{-1}): $\nu_{C\equiv C}$ 2134 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.20 (t, $^{3}J_{HH}$ = 6.8 Hz, 2H, CH$_2$CH_2N), 2.87 (m, 2H, CH_2CH$_2$N), 2.29 (s, 6H, NMe_2), 2.02 (t, $^{4}J_{HH}$ = 2.6, 1H, CH).

Synthesis of H–C≡CCH$_2$CH$_2$(C$_5$H$_5$N) (5)

A solution of 2-picoline (4.7 g, 50.4 mmol) in methyl-*tert*-butyl ether (60 mL) was treated with phenyllithium (36.0 mL, 1.4 M in cyclohexane–ether) and stirred for 1 h at 0°C to yield a pale orange solution. Thereafter, 3-bromopropyne (6.0 g, 50.4 mmol) was added within 10 min and the mixture refluxed for 1 h. A sodium carbonate aqueous solution (1 g/100 mL) was then added and the organic phase separated. The aqueous phase was washed with methyl-*tert*-butyl ether (3 × 100 mL) and the organic phase dried with $MgSO_4$, filtered and evaporated to dryness. The final residue was chromatographed on silica gel using a mixture of hexane and ethyl acetate (10:1). Yield (1.32 g, 20%). IR (NaCl film, cm^{-1}): $\nu_{C\equiv C}$ 2117. ^{1}H NMR ($CDCl_3$): δ 8.57 (d, 1H, $^{3}J_{HH}$ = 5.2, H_oPy), 7.64 (t, 1H, $^{3}J_{HH}$ = 5.2, H_pPy),

7.23 (m, 2H, H_mPy), 3.04 (t, 2H, $^3J_{HH}=7.3$, CH_2Py), 2.69 (t, 2H, $^3J_{HH}=7.3$, $^4J_{HH}=2.7$, CH_2CH_2Py), 1.99 (t, $^4J_{HH}=2.7$, 1H, CH).

General Procedure for the Preparation of Five-Coordinate Vinyl-Ruthenium Compounds

A solution of **1** (100 mg, 0.21 mmol) in toluene (10 mL) was treated with propargyl amine (**2–5**) (0.23 mmol). After stirring for 4 h at room temperature the solution was concentrated and hexane (40 mL) was added resulting in the formation of a dark solid which was filtered in celite and the clear solution evaporated to dryness.

[RuCl(CH=CHCH$_2$NMe$_2$)(CO)(PiPr$_3$)$_2$] (**6**) **6** was obtained as a rose-colored solid (108 mg, 95%). IR (KBr, cm^{-1}): ν_{CO} 1905, $\nu_{C=C}$ 1584. Anal. Calcd for $C_{24}H_{52}ClNOP_2Ru$: C, 50.65; H, 9.21; N, 2.46. Found: C, 50.77; H, 9.57; N, 2.53. ^{1}H NMR ($CDCl_3$): δ 7.39 (d, 1H, $^3J_{HH}=12.4$, RuC*H*=CH), 4.99 (m, 1H, RuCH=C*H*), 2.91 (d, 2H, $^3J_{HH}=6.9$, CH_2), 2.73 (m, 6H, *CH*Me$_2$), 2.14 (s, 6H, NMe$_2$), 1.27 (m, 36H, CH(*CH*$_3$)$_2$). ^{13}C{^{1}H}($CDCl_3$): δ 202.3 (t, Ru*C*O), 145.1 (t, Ru*C*H=CH), 138.2 (s, RuCH=*C*H), 64.6 (s, =*C*CH$_2$), 44.7 (s, N*C*H$_3$), 24.2 (t, *C*HMe$_2$), 19.9, 18.9 (s, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR: δ 37.34.

[RuCl{CH=CHCH$_2$N(Me)(CH$_2$Ph)}(CO)(PiPr$_3$)$_2$] (**7**) **7** was obtained as a rose-colored oil (101 mg, 78%). IR (NaCl film, cm^{-1}): ν_{CO} 1905, $\nu_{C=C}$ 1581. Anal. Calcd for $C_{30}H_{56}ClNOP_2Ru$: C, 55.84; H, 8.75; N, 2.17. Found: C, 54.97; H, 8.87; N, 2.11. ^{1}H NMR ($CDCl_3$): δ 7.44 (d, 1H, $^3J_{HH}=12.7$, RuC*H*=CH), 7.29 (m; 5H, Ph), 5.15 (m, 1H, RuCH=C*H*), 3.07 (d, 2H, $^3J_{HH}=6.6$, CH_2), 2.75 (m, 6H, *CH*Me$_2$), 2.09 (s, 6H, NMe$_2$), 1.30 (m, 36H, CH(*CH*$_3$)$_2$). ^{13}C{^{1}H} ($CDCl_3$): δ 202.8 (t, Ru*C*O), 144.9 (t, Ru*C*H=CH), 139.6 (s, RuCH=*C*H), 131.1, 129.0, 128.2, 126.8 (phenyl ring), 63.0 (s, *C*H$_2$Ph), 60.1 (s, =*C*CH$_2$), 41.2 (s, N*C*H$_3$), 24.3 (t, *C*HMe$_2$), 19.9, 18.9 (s, CH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR: δ 37.21.

[RuCl(CH=CHCH$_2$CH$_2$Py)(CO)(PiPr$_3$)$_2$] (**8**) **8** was obtained as a rose-brown oil. (90.1 mg, 71%). IR (NaCl film, cm^{-1}): ν_{CO} 1903, $\nu_{C=C}$ 1586. Anal. Calcd for $C_{28}H_{52}ClNOP_2Ru$: C, 54.44; H, 8.42; N, 2.27. Found: C, 54.28; H, 9.02; N, 2.09. ^{1}H NMR ($CDCl_3$): δ 8.53 (d, 1H, $^3J_{HH}=5.2$, H_oPy), 7.61 (t, 1H, $^3J_{HH}=5.2$, H_pPy), 7.30 (m, 3H, H_mPy and RuC*H*=CH), 5.13 (m, 1H, RuCH=C*H*), 2.80 (m, 8H, CH_2Py and *CH*Me$_2$), 2.55 (t, 2H, $^3J_{HH}=7.1$, CH_2CH_2Py), 1.30 (m, 36H, CH(*CH*$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 202.1 (t, Ru*C*O), 151.7 (s, CH-1-Py), 146.2 (t, Ru*C*H=CH), 144.2 (C_{ipso}-Py) 140.1 (s, RuCH=*C*H), 136.4 (s, CH-3-Py), 126.3 (s, CH-4-Py),

123.8 (s, CH-2-Py), 64.2 (s, CH_2Py), 61.5 (s, $=CCH_2$), 24.1 (t, $CHMe_2$), 19.4, 18.3 (s, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR: δ 37.42.

[RuCl(CH=CHCH$_2$CH$_2$NMe$_2$)(CO)(PiPr$_3$)$_2$] (**9**) **9** was obtained as a light rose solid. (97 mg, 79%). IR (KBr, cm^{-1}): ν_{CO} 1908, $\nu_{C=C}$ 1584. Anal. Calcd for $C_{25}H_{54}ClNOP_2Ru$: C, 51.49; H, 9.33; N, 2.40. Found: C, 51.20; H, 9.64; N, 2.53. ^1H NMR (300 MHz, $CDCl_3$): δ 7.26 (d, 1H, $^3J_{HH}$ = 12.7, RuC*H*=CH), 4.88 (m, 1H, RuCH=C*H*), 3.93 (t, $^3J_{HH}$ = 6.6 Hz, 2H, $=CH_2CH_2N$), 2.90 (s, 6H, NMe_2), 2.76 (m, 6H, $CHMe_2$), 2.39 (m, 2H, $=CH_2CH_2N$), 1.30 (m, 36H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ ($CDCl_3$): δ 203.0 (t, Ru*C*O), 142.0 (t, Ru*C*H=CH), 128.0 (s, RuCH=*C*H), CH_2NMe_2 (not observed), 65.8 (s, $=CCH_2$), 35.6 (s, NCH_3), 24.4 (t, $CHMe_2$), 19.9, 18.7 (s, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR: δ 37.47.

{RuCl[(CH=CHCH$_2$N(Me)(CH$_2$Ph)](CO)$_2$(PiPr$_3$)$_2$} (**10**) To a toluene solution of **7** (0.14 mmol, 20 mL), carbon monoxide was bubbled for 15 min at room temperature. The resulting pale yellow solution was filtered and the solvent pumped off to yield a yellow oil which was recrystallized from CH_2Cl_2–hexane at −20°C yielding **10** as a pale yellow oil (75 mg, 89%). IR (KBr, cm^{-1}): ν_{CO} 2012; 1941, $\nu_{C=C}$ 1592. Anal. Calcd for $C_{31}H_{56}ClNO_2P_2Ru$: C, 55.30; H, 8.38; N, 2.08. Found: C, 55.42; H, 8.27; N, 2.11. ^1H NMR ($CDCl_3$): δ 7.32 (d, 1H, $^3J_{HH}$ = 16.7, RuC*H*=CH), 7.21 (m; 5H, Ph), 5.68 (m, 1H, RuCH=C*H*), 3.19 (s, 2H, CH_2N), 2.72 (m, 6H, $CHMe_2$), 2.27 (s, 6H, NMe_2), 1.33 (m, 36H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ ($CDCl_3$): δ 202.0; 197.4 (t, Ru*C*O), 158.2 (t, Ru*C*H=CH), 139.8 (s, RuCH=*C*H), 129.5, 128.7, 127.6, 126.9 (phenyl ring), 67.9 (s, CH_2Ph), 62.1 (s, $=CCH_2$), 42.1 (s, NCH_3), 25.2 (t, $CHMe_2$), 20.7, 19.8 (s, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR: δ 36.03.

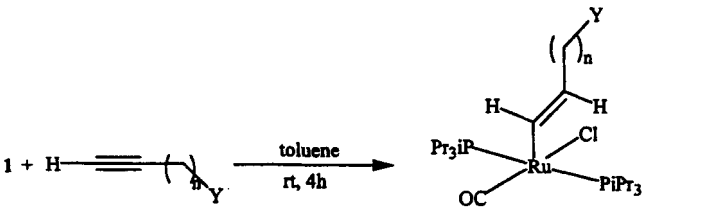
RESULTS AND DISCUSSION

The propargyl amines H−C≡CCH$_2$CH$_2$Y (**4**, Y = NMe_2; **5**, Y = Py) were synthesized by methods described in the literature.[9] Thus the functionalized alkyne **4** was prepared by treatment of the corresponding mesylated hydroxyl group of the 3-butyn-1-ol with an excess of dimethyl amine and isolated as a colorless oil in 68% yield. Compound **5** was obtained by lithiation of 2-picoline followed by reaction with 3-bromopropyne affording **5** as a yellowish oil in 20% yield. Compounds **4**–**5** were characterized by IR and NMR spectroscopy. The IR spectra of the propargyl amines **4**–**5** show one medium intensity band at 2134 and 2117 cm^{-1} corresponding to ν(C≡C).

Hydroruthenation to synthesize the vinyl compounds (**6–9**), involves the simple reaction of the propargyl amine ligands (**2–5**) and [RuHCl(CO)-($P i Pr_3$)$_2$] (**1**) using toluene as solvent. Thus the reaction between **1** and the propargyl amines (**2–5**) at room temperature in toluene for 4 h afforded the five-coordinate vinyl-complexes {RuCl[(*E*)–CH=CH(CH$_2$)$_n$Y](CO)-($P i Pr_3$)$_2$} (**6**, Y = NMe$_2$, $n = 1$; **7**, Y = N(Me)CH$_2$Ph, $n = 1$; **8**, Y = Py, $n = 2$; **9**, Y = NMe$_2$, $n = 2$), respectively (Scheme 1).

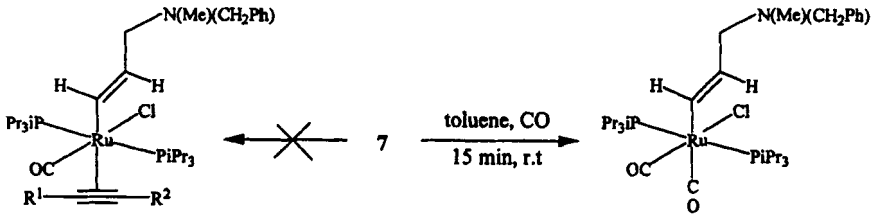
The five-coordinate vinyl-complexes **6–9** are air-stable and can be isolated in good yields (70–75%) as rose solids or brown yellow oils. The structures of **6–9** are assigned based on elemental analysis, IR and multinuclear (^{1}H, ^{13}C, ^{31}P) NMR data. In the IR spectra of complexes **6–9**, the absence of IR bands in the region of 2300–2100 cm^{-1}, attributed to ν(C≡C), and the presence of one medium intensity band around 1586 cm^{-1} corresponding to ν(C=C), indicate the formation of vinyl complexes. As expected, the IR spectra show one intense band of carbonyl stretching near 1904 cm^{-1}. Similar carbonyl stretching frequencies found for all vinyl compounds (**6–9**), point out that the presence of different types of vinyl units coordinated to the ruthenium atom do not change the electronic density around the metal center. In the ^{1}H NMR spectra of **6–9**, the *trans* stereochemistry at the C=C bond is strongly supported by the large proton–proton coupling constant, which is in the range 12–13 Hz.[10] In the ^{13}C{^{1}H} NMR spectra of the vinyl complexes, the triplet signal at 202 ppm is attributed to the carbonyl group and the carbons of the vinyl fragment (Ru–C=C–) appear at 142 and 128 ppm. The ^{31}P{^{1}H} NMR spectra show singlets of about 37 ppm, indicating that the two phosphine ligands are equivalent.

Although compounds **6–9** are coordinatively unsaturated, their reaction with alkynes such as 1-dimethylamino-2-propyne, acetylenedicarboxylic



6, Y = NMe$_2$, n = 1
7, Y = N(Me)CH$_2$Ph, n = 1
8, Y = Py, n = 2
9, Y = NMe$_2$, n = 2

SCHEME 1



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SCHEME 2

acid and phenylacetylene fail even at higher temperatures and/or using an excess of alkyne ligand (Scheme 2). Similar results have been obtained from reaction of **1** with olefins.[8] Conversely, CO can be added to the five-coordinate vinyl-compounds (**6–9**). In a typical reaction, carbon monoxide was bubbled through the orange toluene solution of **7** where within 15 min the solution became pale yellow. The solvent was pumped off and the resulting yellow oil was purified yielding **10** as a pale yellow oil in 89% yield (Scheme 2). The IR spectrum of **10** shows two intense bands at 2012 and 1941 cm^{-1} indicating a *cis*-dicarbonyl geometry. The ^1H NMR spectrum shows peaks corresponding to a vinyl group shifted upfield, beside those related to the phosphine ligands. The $^{13}C\{^1H\}$ NMR spectrum shows two triplet signals at 202.0 and 197.4 ppm attributed to the *cis* carbonyl ligands position in agreement with the results obtained from the IR spectrum.

CONCLUSION

The results of the present work demonstrate that the five-coordinated vinyl-compounds (**6–9**) and hexacoordinated (**10**) containing a nitrogen group can be easily synthesized, in good yields, by hydroruthenation reactions followed by reaction with carbon monoxide. Furthermore, the presence of a potentially coordinating nitrogen group attached to vinyl moiety allows the extension of these studies towards the synthesis of heterometallic compounds. We are currently pursuing this.

Acknowledgments

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