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Communications

C_5H_5-Bridged Dimeric Ruthenium Complexes

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Summary: Reaction of $HC\equiv CCH(OH)C\equiv CH$ *with* $RuHCl(CO)(PPh_3)_3$ *leads to the isolation of the* C_5H_5*-bridged complex* $(PPh_3)_2(CO)ClRuCH{=}CH\text{-}CH{=}CHCH{=}RuCl(OH)(CO)(PPh_3)_2$ (**2**). *The* C_5H_5*-bridged complex* **2** *reacted with* PMe_3 *and dppe to give* $[(PMe_3)_3(CO)ClRuCH{=}CHCH(PMe_3)CH{=}CHRuCl(CO)(PMe_3)_3]OH$ *and* $(PPh_3)(dppe)(CO)ClRuCH{=}CHCH{=}CHCH{=}RuCl(OH)(CO)(PPh_3)_2$*, respectively.*

Dimeric organometallic compounds with π-conjugated bridges have recently attracted considerable attention, because of their unusual intrinsic chemical, physical, and material properties.[1,2] Some of the most interesting conjugated organometallic dimeric complexes reported recently include those with C_x-bridged complexes $L_nMC_xM'L_n'$ (e.g. $[Cp^*Re(NO)(PPh_3)(\mu\text{-}C_5)Mn(CO)_2(C_5Cl_5)]^+$),[3,4] C_4R_2-bridged complexes with $M\equiv C$ linkages such as $[(Me_3SiNCH_2CH_2)_3N]Mo\equiv CCH{=}CHC\equiv Mo[N(CH_2CH_2NSiMe_3)_3]$[5] or complexes with $M{=}C$ linkages such as $[(C_5H_4SiMe_3)_2(CO)Nb{=}C{=}CMeCMe{=}C{=}Nb(CO)(C_5H_4SiMe_3)_2](BPh_4)_2$,[6] and 1,3-bimetalated cyclobutenylidene (C_4R_3) complexes.[7] Although on the one hand a large number of conjugated dimeric organometallic complexes have been synthesized and on the other hand many conjugated organic materials (for example, polyacetylenes, push/pull stilbenes and polyenes) have only sp^2 carbons in their backbones,[8] only a few dimeric

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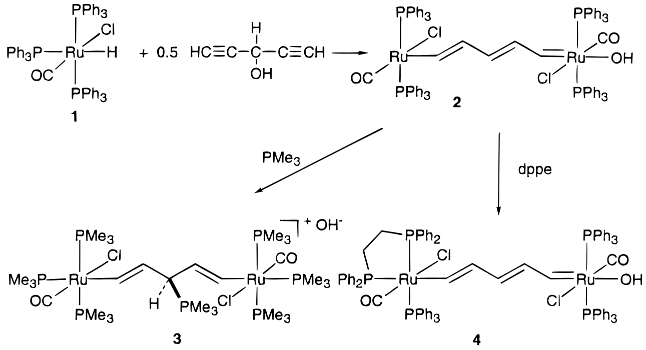
complexes with C_nH_n bridges have been reported. Complexes with C_nH_n bridges are limited to complexes with a C_2H_2 bridge (e.g. $Cp_2ClZrCH=CHRu(PPh_3)_2Cp$, (TMP)RuCH=CHRu(TMP) (TMP = tetramesitylporphyrin)),[9,10] C_4H_4 bridge (e.g. [Cp(LL′)FeCH=CH-CH=CHFe(LL′)Cp] (LL′ = dppm, $(CO)_2$, $(CO)(PMe_3)$, $(CO)(PPh_3)$)),[11] and C_6H_6 bridge (e.g. $(DME)((CF_3)_2MeCO)_2(ArN)Mo=CHCH=CHCH=CHCH=Mo(NAr)(OCMe(CF_3)_2)(DME)$).[12] Dimeric complexes bridged with $(CH)_x$ where x is odd are still unknown. We are interested in the synthesis and properties of conjugated dimeric and polymeric complexes with $(CH)_x$ bridges. We here report a surprisingly easy method to prepare the first C_5H_5-bridged dimeric complexes. Reported complexes close to the C_5H_5-bridged complexes are the tetrairon complexes bridged with C_7H_5 and C_5H_3.[13]

Reactions of $RuHCl(CO)(PPh_3)_3$ with terminal acetylenes HC≡CR are known to give $RuCl(CH=CHR)(CO)(PPh_3)_2$.[14] Thus the reaction of HC≡CCH(OH)C≡CH[15] with $RuHCl(CO)(PPh_3)_3$[16] was investigated, hoping that such reaction would produce $(PPh_3)_2(CO)ClRuCH=CHCH(OH)CH=CHRuCl(CO)(PPh_3)_2$, which can then be converted to $[(PPh_3)_2(CO)ClRuCH=CHCH=CHCH=RuCl(CO)(PPh_3)_2]^+$ by electrophillic abstraction of the OH group. Addition of HC≡CCH(OH)C≡CH to a suspension of $RuHCl(CO)(PPh_3)_3$ (**1**) in CH_2Cl_2 led to an immediate reaction to give a red solution. Removal of CH_2Cl_2 followed by extraction of the residue with benzene produced a purple solution, from which a purple solid can be obtained using ether as the precipitating solvent. The analytical and spectroscopic data indicate that the isolated product is in fact the C_5H_5-bridged complex $(PPh_3)_2(CO)ClRuCH=CHCH=CHCH=RuCl(OH)(CO)(PPh_3)_2$ (**2**), instead of the expected simple insertion product (see Scheme 1). Related mononuclear complexes $(PPh_3)_2(CO)ClRuCH=CHR$[14] and $(P\text{-}i\text{-}Pr_3)_2(CO)Cl_2M=CH\text{-}CH=CRR'$ (M = Ru, Os)[17a,b] and $(PCy_3)_2Cl_2Ru=CHCH=CRR'$ [17c] are known.

Scheme 1



Complex **2** is likely formed from the intermediate $(PPh_3)_2(CO)ClRuCH=CHCH(OH)CH=CHRuCl(CO)(PPh_3)_2$. Although we have not been able to isolate the latter compound yet, it has been reported[17a] that reactions of HC≡CC(OH)RR′ with $RuHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ produced $RuCl(CH=CHC(OH)RR')(CO)(P\text{-}i\text{-}Pr_3)_2$. It is also known that the vinyl carbene complexes $(P\text{-}i\text{-}Pr_3)_2(CO)Cl_2Os=CHCH=CPhR$ were produced from the reactions of $OsHCl(CO)(P\text{-}i\text{-}Pr_3)_2$ with HC≡CC(OH)PhR (R = H, Ph) *via* the vinyl intermediates $(P\text{-}i\text{-}Pr_3)_2(CO)ClOsCH=CHC(OH)PhR$.[17b] In our case, formation of $(PPh_3)_2(CO)ClRuCH=CHCH=CHCH=RuCl_2(CO)(PPh_3)_2$ from the reaction of HC≡CCH(OH)C≡CH with $RuHCl(CO)(PPh_3)_3$ is also possible; however, formulation of the product as complex **2** is more consistent with the spectroscopic data.

Compound **2** was characterized by elemental analysis, IR, UV/vis, and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.[18] The presence of the $Ru_2(\mu\text{-}C_5H_5)$ assembly in **2** is confirmed by the ^1H NMR (in $CDCl_3$) which showed resonances assignable to the five CH signals at 13.64 (Ru=CH), 6.45 (Ru=CHC*H*), 5.53 (RuCH=CHC*H*), 5.80 (RuCH=C*H*), and 11.14 ppm (RuCH). The observation of $^3J(HH)$ coupling constants larger than 12 Hz indicates that all the vinylic protons are *trans* to each other.[12] The observation of signals of the CH groups bound to ruthenium at down-field (>10 ppm) clearly indicates the presence of a Ru=CH linkage[19] and the contribution to the structure from resonance structures such as **2** and **2A**. For comparison, the signals for Ru=CH were observed at 19.06 ppm (d, $J(HH) = 10.5$ Hz) for $RuCl_2$-

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[18] Preparation of **2**: To a suspension of $RuHCl(CO)(PPh_3)_3$ (0.476 g, 0.500 mmol) in 30 mL of CH_2Cl_2 was added HC≡CCH(OH)C≡CH (20 mg, 0.250 mmol). The reaction mixture was stirred for 15 min to give a red solution. The solvent was removed under vacuum, and the residue was extracted with 20 mL of benzene to give a purple solution. Addition of ether (150 mL) to the solution gave a purple solid which was collected by filtration, washed with ether and hexane, and dried under vacuum. Yield: 0.28 g, 76%. $^{31}P\{^1H\}$NMR (CD_2Cl_2): δ 28.9 (s), 19.5 (s). ^1H NMR ($CDCl_3$): δ 13.64 (d, $^3J(HH) = 12.9$ Hz, 1 H, Ru=CH), 11.14 (d, $^3J(HH) = 12.6$ Hz, 1 H, RuCH), 7.83–7.07 (m, Ph), 6.45 (t, $^3J(HH) = 13.3$ Hz, 1 H, Ru=CHC*H*), 5.80 (t, $^3J(HH) = 11.7$, 1 H, RuCH=C*H*), 5.53 (t, $^3J(HH) = 12.1$ Hz, 1 H, RuCH=CHC*H*), 1.58 (br, OH). The ^1H NMR assignments are based on a $^1H-^1H$ COSY experiment. IR (KBr, cm^{-1}): 3445 (br, ν(OH), 1940 (s, $\omega_{1/2} = 45$ cm^{-1}, ν(CO)). Two ν(CO) bands are expected for the complex. It is possible that the two ν(CO) bands are overlapped in the IR spectrum. UV/vis (CH_2Cl_2): λ_{max} (ϵ) = 230 (7.9×10^4 M^{-1} cm^{-1}), 535 nm (4.2×10^4 M^{-1} cm^{-1}). Anal. Calcd for $Ru_2C_{79}H_{66}Cl_2O_3P_4$: C, 64.98; H, 4.56. Found: C, 64.59; H, 5.04.

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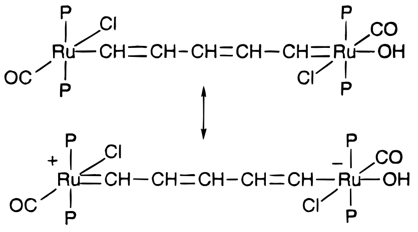

2

2A

P = PPh_3

$(PCy_3)_2(=CHCH=CH_2)$[17c] and at 16.67 ppm (d, J(HH) = 13.4 Hz) for $RuCl_2(P\text{-}i\text{-}Pr_3)_2(=CHCH=CHPh)$;[17a] the signals for RuCH in $RuCl(CO)(P\text{-}i\text{-}Pr_3)_2(CH=CHCH(OH)R)$ were observed at 7.75 ppm (d, J(HH) = 12.8 Hz) for R = H and 7.70 ppm (d, J(HH) = 11.4 Hz) for R = Ph.[17a] The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 showed two singlets at 28.9 and 19.5 ppm, indicating that compound **2** has two different ruthenium centers with mutually *trans* PPh_3 ligands. The presence of the OH group is supported by the elemental analysis and the presence of a broad band around 3445 cm^{-1} assignable to ν(OH) in the IR spectrum. Furthermore, a broad signal at 1.58 ppm assignable to OH was observed in the ^1H NMR spectrum (in $CDCl_3$). However, it should be mentioned that the broad OH signal may be the averaging signals of the OH in the ruthenium complexes and that of residual water in the deuterated solvent. Thus all the spectroscopic data are consistent with the structure shown in Scheme 1, although the alternative geometrical isomer in which the OH is *cis* to the bridge cannot be excluded. Unfortunately, a good ^{13}C NMR spectrum of compound **2** could not be obtained due to its poor solubility in common organic solvents.

In a hope to obtain more soluble C_5H_5-bridged dimeric complexes, it was attempted to substitute PPh_3 from complex **2** with PMe_3 or dppe. Surprisingly, complex **2** reacted with excess PMe_3 to give the white complex $[(PMe_3)_3(CO)ClRuCH=CHCH(PMe_3)CH=CHRuCl(CO)(PMe_3)_3]OH$ (**3**).[20] Thus attack on the γ-carbon of the C_5H_5 unit by PMe_3 occurred. The addition of PMe_3 to the γ carbon of the C_5H_5 unit is similar to the reactions of phosphines with certain allenylidene complexes.[21] For example, $[(\eta^5\text{-}C_9H_7)(PPh_3)_2Ru=C=C=CPh_2]PF_6$ reacted with PMe_3 to give $[(\eta^5\text{-}C_9H_7)(PPh_3)_2Ru\text{-}C{\equiv}C\text{-}C(PMe_3)Ph_2]PF_6$.[22]

The presence of $RuCH=CHCH(PMe_3)CH=CHRu$ in **3** is supported by the ^1H, ^{13}C, and ^{31}P NMR spectroscopic data. The ^1H NMR spectrum (in CD_2Cl_2) showed resonances for the vinyl protons at 7.41 and 5.39 ppm and the resonance for the central CH at 3.62 ppm. The $^{13}C\{^1H\}$ NMR spectrum (in CD_2Cl_2) showed a RuCO resonance at 201.8 ppm (q, ^2J(PC) = 12.3 Hz) and $RuCH=CH$ resonances at 169.8 (dt, ^2J(PC) = 79.2, 12.8 Hz, RuCH) and 110.0 ppm (s, $RuCH=\mathit{C}H$). The ^{13}C NMR data indicate that both the CO and vinyl ligands are *cis* to the three phosphorus atoms. The signal of the central CH carbon was observed at 51.6 ppm with ^1J(PC) = 40.8 Hz and ^4J(PC) = 8.2 Hz. In the $^{31}P\{^1H\}$ NMR spectrum (in CD_2Cl_2) the resonance for the PMe_3 attached on the central carbon atom was observed at 24.9 ppm with long-range ^5J(PP) = 7.7 Hz. For comparison, the chemical shift of $[Me_3P\text{-}c\text{-hexyl-4-Me})]^+$ is 30 ppm and that of $[Me_3P(7\text{-}Nb)]I$ (Nb = norbornyl) is 24.2 ppm.[23] The resonances for the PMe_3 ligands coordinated on ruthenium were observed at −8.2 (dd, ^2J(PP) = 25.3 Hz, ^5J(PP) = 7.7 Hz) and −19.6 ppm (t, ^2J(PP) = 25.3 Hz). In principle, the two *trans* PMe_3 groups in **3** are inequivalent due to the presence of PMe_3 at the central carbon atom and should give distinguishable signals in the ^1H, ^{13}C, and ^{31}P NMR spectra. The subtle difference is indicated by its ^{13}C NMR but not by its ^1H and ^{31}P NMR.

Reaction of complex **2** with dppe led to partial substitution of PPh_3 to give the C_5H_5-bridged complex $(PPh_3)(dppe)(CO)ClRuCH=CHCH=CHCH=RuCl(OH)(CO)(PPh_3)_2$ (**4**).[24] The presence of a $Ru_2(\mu\text{-}C_5H_5)$ assembly is confirmed by the ^1H and $^{13}C\{^1H\}$ NMR (in $CDCl_3$). In the ^1H NMR spectrum the signals due to the C_5H_5 unit were observed at 13.98 (Ru=CH), 6.57 ($Ru=CHC\mathit{H}$), 5.74 ($RuCH=CHC\mathit{H}$), 5.95 ($RuCH=C\mathit{H}$), and 11.00 ppm (Ru-CH). The $^{13}C\{^1H\}$ NMR showed resonances assignable to the C_5H_5 unit at 304.8 (t, J(PC) = 7.7 Hz, Ru=CH), 231.2 (dt, J(PC) = 74.4, 11.8 Hz, RuCH), 149.7 (d, ^4J(PC) = 6.3 Hz, CH(γ)), 142.3 (s), and 141.6 ppm (s). For comparison, the ^{13}C signals for Ru=CH were observed at 296.00 ppm (t, J(PC) = 7.6 Hz) for $RuCl_2(PCy_3)_2(=CHCH=CH_2)$[17c] and at 314.48 ppm (t, J(PC) = 8.7 Hz) for $RuCl_2(P\text{-}i\text{-}Pr_3)_2(=CHCH=CPh_2)$;[17a] the signal for RuCH in $Ru(H_2B(bta)_2)(CO)(PPh_3)_2(CH=CH\text{-}n\text{-}Bu)$ (bta = benzotriazol-1-yl) was observed at 145.2 ppm (t, J(PC) = 12.8 Hz).[14f] The presence of only one dppe ligand in complex **4** has been confirmed by its $^{31}P\{^1H\}$ NMR and $^{31}P\{^1H\}-^1H$ correlation spectra. The presence of the OH group is consistent with the elemental analysis and the presence of a broad band around 3500 cm^{-1} assignable to ν(OH) in the IR spectrum.

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(20) Preparation of **3**: To a purple solution of **2** (0.300 g, 0.205 mmol) in 20 mL of CH_2Cl_2 was added 3 mL of a 1 M THF solution of PMe_3. The reaction mixture was stirred for 15 min to give a colorless solution. The volume of the reaction mixture was reduced to *ca.* 2 mL under vacuum, and 15 mL of ether was added to give a white solid. The solid was collected by filtration, washed with ether and hexane, and dried under vacuum. Yield: 0.14 g, 72%. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 24.9 (quintet, ^5J(PP) = 7.7 Hz), −8.2 (dd, ^2J(PP) = 25.3 Hz, ^5J(PP) = 7.7 Hz), −19.6 (t, ^2J(PP) = 25.3 Hz). ^1H NMR (CD_2Cl_2): δ 7.41 (dm, ^3J(HH) = 12.7 Hz, 2H, RuCH), 5.39 (dd, ^3J(HH) = 6.4, 12.7 Hz, 2 H, $RuCH=C\mathit{H}$), 3.62 (dt, ^3J(HH) = 6.4 Hz, ^2J(PH) = 14.5 Hz, 1 H, $C\mathit{H}PMe_3$), 3.4 (br, OH), 2.06 (d, ^2J(PH) = 13.5 Hz, $CHP\mathit{Me}_3$), 1.43 (d, J(PH) = 7.0 Hz, 18 H, 2 PMe_3), 1.40 (t, J = 3.3 Hz, 36 H, 4 PMe_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 201.8 (q, ^2J(PC) = 12.3 Hz, RuCO), 169.8 (dt, ^2J(PC) = 79.2, 12.8 Hz, RuCH), 110.0 (s, $RuCH=\mathit{C}H$), 51.6 (dt, ^1J(PC) = 40.8, ^4J(PC) = 8.2 Hz, $\mathit{C}HPMe_3$), 19.3 (d, ^1J(PC) = 21.9 Hz, PMe_3), 16.8 (t, J = 15.4 Hz, PMe_3), 16.5 (t, J = 15.4, PMe_3), 7.4 (d, ^1J(PC) = 53.1 Hz, $CHP\mathit{Me}_3$). The ^{13}C and ^1H NMR assignments are based on ^{13}C DEPT and 2D NMR experiments ($^1H-^1H$, $^1H-^{13}C$, $^1H-^{31}P$ COSY). Anal. Calcd for $Ru_2C_{28}H_{69}Cl_2O_3P_7$: C, 35.64; H, 7.37. Found: C, 35.55; H, 7.31.

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(24) Preparation of **4**: To a purple solution of **2** (0.300 g, 0.205 mmol) in 20 mL of CH_2Cl_2 was added dppe (0.40 g, 1.0 mmol). The reaction mixture was stirred for 30 min to give a purple solution. The volume of the reaction mixture was reduced to *ca.* 2 mL under vacuum, and 50 mL of ether was added to give a purple solid. The solid was collected by filtration, washed with ether and hexane, and dried under vacuum. Yield: 0.28 g, 86%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 42.3 (dd, J(PP) = 288.0, 5.7 Hz, PPh_2), 26.7 (dd, J(PP) = 21.3, 5.7 Hz, PPh_2), 23.4 (dd, J(HH) = 288.0, 21.3 Hz, PPh_3), 20.1 (s, PPh_3), 20.0 (s, PPh_3). ^1H NMR ($CDCl_3$): δ 13.98 (dt, ^3J(HH) = 13.5 Hz, J(PH) = 2.3 Hz, 1 H, Ru=CH), 11.0 (m, 1 H, RuCH), 6.57 (t, ^3J(HH) = 13.4 Hz, 1 H, $Ru=CHC\mathit{H}$), 5.95 (m, 1 H, $RuCH=C\mathit{H}$), 5.74 (t, ^3J(HH) = 12.1 Hz, 1 H, $RuCH=CH\text{-}C\mathit{H}$), 8.01−7.02 (m, Ph), 2.4−2.7 (m, 4 H, CH_2), 1.61 (br, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 304.8 (t, ^2J(PC) = 7.7 Hz, Ru=CH), 231.2 (dt, ^2J(PC) = 74.4, 11.8 Hz, RuCH), 199.5−200.1 (m, RuCO), 149.7(d,

We have attempted to prepare the symmetric complex $[(PPh_3)_2(CO)ClRuCH{=}CHCH{=}CHCH{=}RuCl(CO)(PPh_3)_2]^+$ by treatment of **2** with $HBF_4{\cdot}Et_2O$. A predominant phosphorus-containing species was produced. Unfortunately, the product appears unstable and we have not been able to purify and fully characterize the product yet.

The C_5H_5 complexes have an intense purple color. In the UV/vis spectrum of complex **2** strong absorption bands at 230 ($\epsilon = 7.9 \times 10^4$ M^{-1} cm^{-1}) and 535 nm ($\epsilon = 4.2 \times 10^4$ M^{-1} cm^{-1}) were observed. In the UV/vis spectrum of complex **4** strong absorption bands at 229 ($\epsilon = 7.2 \times 10^4$ M^{-1} cm^{-1}) and 530 nm ($\epsilon = 1.3 \times 10^4$ M^{-1} cm^{-1}) were observed. The band around 230 nm can be assigned to electronic transitions involving Ph groups of the phosphine ligands, and the band around 530 nm could be associated with $Ru_2(\mu\text{-}C_5H_5)$.

In summary, we have developed a simple method to prepare interesting conjugated C_5H_5-bridged complexes. The γ-position of the C_5H_5 unit appears reactive toward nucleophiles. We are in the process of investigating the mechanism for the formation of **2** and extending the chemistry to prepare other $(CH)_x$-bridged dimeric and polymeric complexes.

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$^4J(PC) = 6.3$ Hz, CH(γ)), 142.3 (s, CH), 141.6 (s, CH), 134.4−127.3 (m, Ph), 30.3−30.9 (m, CH_2), 25.2−25.8 (m, CH_2). The ^{13}C and ^1H NMR assignments are based on ^{13}C DEPT and 2D NMR experiments ($^1H-^1H$, and $^1H-^{13}C$ COSY). IR (KBr, cm^{-1}): 3500 (br, ν(OH), 1946 (s, $\omega_{1/2} = 50$ cm^{-1}, ν(CO)). Two ν(CO) bands are expected for the complex. It is possible that the two ν(CO) bands are overlapped in the IR spectrum. UV/vis (CH_2Cl_2): λ_{max} (ϵ) = 229 (7.2×10^4 M^{-1} cm^{-1}), 530 nm (1.3×10^4 M^{-1} cm^{-1}). Anal. Calcd for $Ru_2C_{87}H_{75}Cl_2O_3P_5$: C 65.46; H, 4.74. Found: 65.29, H, 4.80.

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