Condensation of Os(CO)4(.eta.2-HCCH) with CpRh(CO)(PR3). Unexpected phosphine dependence in the formation of dimetallacycles: reverse regiochemistry and a zwitterionic compound

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Condensation of $Os(CO)_4(\eta^2\text{-}HCCH)$ with $CpRh(CO)(PR_3)$. Unexpected Phosphine Dependence in the Formation of Dimetallacycles: Reverse Regiochemistry and a Zwitterionic Compound

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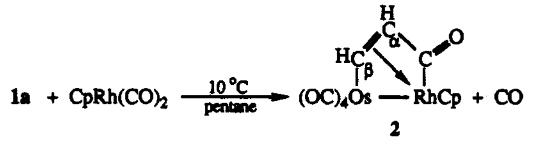
Summary: The reaction of $Os(CO)_4(\eta^2\text{-}HCCH)$ with $CpRh(CO)(PR_3)$ ($PR_3 = PMe_3, PMe_2Ph, PMePh_2$; $Cp = C_5H_5$) yields heterodimetallic compounds, but rather unexpectedly, two different types of complexes are obtained, dependent on the phosphine ligand. One compound class containing $[\mu\text{-}\eta^3\text{:}\eta^1\text{-}C(O)C_2H_2]Os(CO)_3\text{-}RhCp(PMe_2Ph)$ (3a) and its $PMePh_2$ analogue (3b) is based upon a dimetallacyclopentenone ring. The second structural type contains $[\mu\text{-}\eta^1\text{:}\eta^2\text{-}HCCH(PMe_3)](\mu\text{-}CO)Os(CO)_3RhCp$ (4) and can be described as a zwitterionic hydrocarbyl-bridged dimetallic species. The molecular structure of 4 has been confirmed by X-ray crystallography. Crystals of 4 belong to the orthorhombic space group $P2_12_12_1$ with $a = 8.093(2)$ Å, $b = 16.116(3)$ Å, $c = 12.959(2)$ Å, $V = 1690(1)$ Å^3, $Z = 4$, $R = 0.050$, and $R_w = 0.060$.

Earlier, the synthesis of $Os(CO)_4(\eta^2\text{-}RCCR)$ (R = H (**1a**), CF_3 (**1b**)) was reported,[1] along with its unprecedented reactivity toward coordinatively saturated organometallic species. This reactivity is an important tool in the synthesis of alkyne-bridged dimetallic compounds. Specifically, the condensation of **1a** with $CpRh(CO)_2$ ($Cp = C_5H_5$) results in the formation of a heterodimetallic complex containing a dimetallacyclopentenone ring[1a] (eq 1). The reaction is regioselective, as only the isomer with the acyl moiety attached to the rhodium center is seen.



(1)

In order to determine the role of the ancillary ligands in the condensation, the reaction of **1a** with $CpRh(CO)(PR_3)$ ($PR_3 = PMe_3, PMe_2Ph, PMePh_2$)[2] was investigated. In all cases, products of formula $Os(CO)_4(C_2H_2)RhCp(PR_3)$ are obtained. Interestingly, while similar complexes were obtained for $PR_3 = PMe_2Ph, PMePh_2$, the use of PMe_3 resulted in a significant structural change. This result was surprising in that a relatively narrow range of phosphines resulted in dramatic product diversity. In addition, the regioselectivity of the condensation is affected by the presence of phosphine substituents.

By the established precedent, the condensation of **1a** with $CpRh(CO)(PR_3)$ ($PR_3 = PMe_2Ph, PMePh_2$) gave dimetallic compounds. The spectroscopic data[3] for the orange products **3a,b** were consistent with the formulation of a dimetallacyclopentenone ring[4] (eq 2).

$$\mathbf{1a} + CpRh(CO)(PR_3) \xrightarrow[\text{pentane}]{10\,^\circ C}$$

$$[\mu\text{-}CHCHC(O)]Os(CO)_3RhCp(PR_3) + CO \quad (2)$$

$$PR_3 = PMe_2Ph,\ \mathbf{3a}$$

$$PR_3 = PMePh_2,\ \mathbf{3b}$$

The large ^{13}C NMR chemical shift difference between the α and β ring carbons indicates that the unsaturated organic unit is bound to a metal center. Specifically, for **3a** the α-carbon appears at 52.8 ppm, while the β-carbon resonates at 156.0 ppm. This can be compared to **2**, where the α- and β-carbon shifts are 44.4 and 115.7 ppm, respectively.[1a] The large chemical shift difference is also mirrored in the ^1H NMR data for **3a**, where the α-proton resonates at 4.72 ppm while the β-proton is dramatically downfield at 8.82 ppm. Finally, the relatively high frequency of the acyl stretching band at 1696 cm^{-1} also

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(3) **3a**: A pentane solution containing 26.2 mg (0.080 mmol) of **1a** and 30.4 mg (0.091 mmol) of $CpRh(CO)(PMe_2Ph)$ was slowly warmed from −78 to 10 °C using a dry-ice/acetone bath. As the temperature neared 0 °C, the original orange color darkened and an orange precipitate began to form. Continued stirring at 10 °C for 1 h resulted in complete reaction, as judged by FT-IR. The volume of solvent was reduced to *ca.* 10 mL and the solution cooled to −78 °C to effect complete precipitation. The precipitate was isolated and washed with cold pentane (3 × 5 mL). The yield was 32.4 mg (64%). The material may be recrystallized from CH_2Cl_2/pentane at −80 °C. A similar procedure was used to synthesize **3b** in 62% yield. Data for **3a** are as follows: IR (CH_2Cl_2; cm^{-1}): ν(CO) 2043 (m), 1968 (s); ν(acyl) 1696 (m). ^1H NMR (360 MHz, CD_2Cl_2, −20 °C; δ): 8.82 (1H, dd, $^2J_{Rh-H} = 18.9$ Hz, $^3J_{H-H} = 6.3$ Hz, H_β), 7.73 (5H, m, Ph), 4.98 (5H, s, Cp), 4.72 (1H, dd, $^3J_{H-H} = 6.3$ Hz, $^3J_{Rh-H} = 6.3$ Hz, H_α), 1.84 (3H, d $^2J_{P-H} = 9.2$ Hz, CH_3), 1.79 (3H, d, $^2J_{P-H} = 9.5$ Hz, CH_3). ^{13}C NMR (90.5 MHz, CD_2Cl_2, 23 °C; δ): 156.0 (dd, $^1J_{Rh-C} = 35.2$ Hz, $^2J_{P-C} = 14.8$ Hz, C_β), 138.9 (d, $^1J_{P-C} = 48.0$ Hz, ipso), 131.3 (d, $^2J_{P-C} = 11.6$ Hz, ortho), 129.9 (s, para), 128.2 (d, $^3J_{P-C} = 9.6$ Hz, meta), 88.5 (s, Cp), 52.8 (s, C_α), 21.3 (d, $^1J_{P-C} = 31.0$ Hz, CH_3), 15.9 (d, $^1J_{P-C} = 31.3$ Hz, CH_3). ^{13}C NMR (90.5 MHz, CD_2Cl_2, −80 °C; δ): 222.4 (acyl), 181.9 (CO), 179.4 (d, $^2J_{Rh-C} = 5.5$ Hz, CO), 175.2 (CO). ^{31}P NMR (81.0 MHz, CD_2Cl_2, 23 °C; δ): 15.5 (d, $^1J_{Rh-P} = 188.4$ Hz). Anal. Calcd for $C_{19}H_{18}O_4OsPRh$: C, 35.97; H, 2.86. Found: C, 35.84; H, 2.71.

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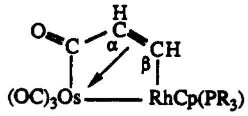
provides evidence for ring coordination. However, and in contrast with 2, the low-field acyl signal in the ^{13}C NMR spectrum lacked ^{103}Rh–^{13}C coupling, thus revealing that the acyl fragment of the ring was bound to the osmium center. Thus, unexpectedly, the condensation reaction proceeds with a regioselectivity reverse to that of previous observations[5] (**A**). The regiochemistry is further corroborated by the observed coupling between Rh and the β-carbon of the dimetallacyclopentenone ring (**3a**: $^1J_{Rh-C}$ = 35.2 Hz).



PR$_3$ = PMe$_2$Ph, PMePh$_2$

A

The reaction of **1a** with CpRh(CO)(PMe$_3$) in pentane solution under mild conditions led to the formation of the ruby red solid **4** (eq 3). Although the molecular composition

$$\mathbf{1a} + \mathrm{CpRh(CO)(PMe_3)} \xrightarrow[\text{pentane}]{10\ ^\circ\mathrm{C}} \underset{\mathbf{4}}{\mathrm{(OC)_4Os(C_2H_2)(PMe_3)RhCp}} + \mathrm{CO} \quad (3)$$

of **4** was identical with that of **3a** and **3b**, its spectroscopic properties were substantially different. The spectroscopic data[6] for **4** did not unambiguously define its structural formulation, but several basic structural features could be inferred from the NMR data. In contrast with an expected[7] one-bond ^{103}Rh–^{31}P coupling of *ca.* 180 Hz (**3a**: $^1J_{Rh-P}$ = 188.4 Hz), the small ^{103}Rh–^{31}P coupling of 10.8 Hz observed for **4** indicated that trimethylphosphine was no longer directly bound to rhodium. This, in addition to the large ^{31}P–^{1}H coupling to both acetylenic hydrogens, strongly implied that the trimethylphosphine ligand in **4** had migrated to the acetylenic moiety. With this information in hand, an X-ray structure determination[8] was undertaken to fully map out the molecular formulation of **4** (Figure 1).

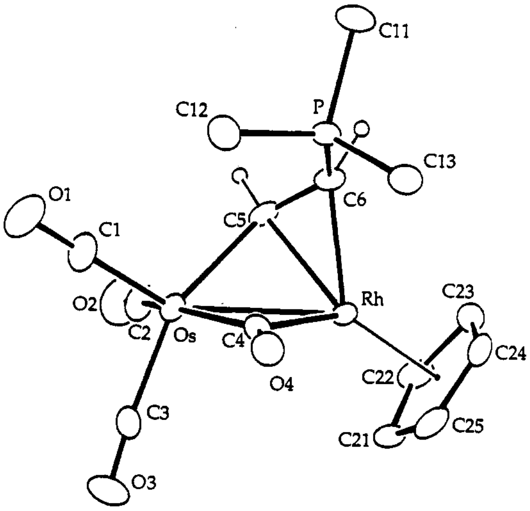
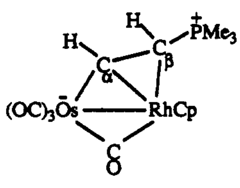
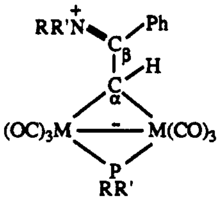


Figure 1. Molecular structure of **4**. Selected bond distances (Å) are as follows: Os–Rh = 2.695(1), Os–C4 = 2.06(1), Os–C5 = 2.13(2), Rh–C4 = 2.04(1), Rh–C5 = 2.10(1), Rh–C6 = 2.15(1), P–C6 = 1.75(1), O4–C4 = 1.16(2), C5–C6 = 1.45(2).

As seen, the PMe$_3$ ligand has indeed migrated from Rh and is now part of a bridging zwitterionic hydrocarbyl moiety with a newly developed phosphonium center and the negative charge on the osmium atom (**B**). The bridging hydrocarbyl ligand is bonded in a μ-η^1:η^2 fashion. The Os–C5, Rh–C5, and Rh–C6 separations are consistent with metal–carbon single bonds. The Os–Rh separation is indicative of a metal–metal single bond, and a bridging carbonyl completes the electronic requirements of both metal centers.

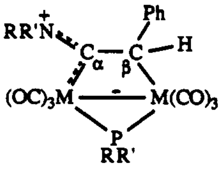


B



M = Fe, Ru, Os

C



M = Fe, Ru, Os

D

The synthesis of a zwitterionic species is not novel, as several groups, most notably those of Carty and Deeming, have reported[9] numerous di- and trimetallic zwitterionic species. However, the classical synthesis of complexes containing two-carbon bridging units involves nucleophilic attack on bridging acetylide ligands. The formation of **4** is unusual, since it appears to involve migration of the nucleophile, PMe$_3$, from a metal center to a bridging acetylene moiety. The structure of **4** is also rare in that the α-carbon bridges both metals and the β-carbon is only attached to one metal center. In previous work, C$_\alpha$-bridged species were limited to μ-alkylidene type complexes (**C**), whereas attachment of C$_\beta$ resulted in rupture of the C$_\alpha$ bridge and formation of metallaphenethylidenes (**D**).

Carty[10] has summarized the ^{13}C NMR chemical shift data for several classes of zwitterionic hydrocarbyl-bridged

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(5) The structure of **3a** has been corroborated by X-ray crystallography.

(6) **4**: A pentane solution containing 27.4 mg (0.084 mmol) of **1a** and 25.1 mg (0.092 mmol) of CpRh(CO)(PMe$_3$) was slowly warmed from −78 °C to 10 °C using a dry-ice/acetone bath. A ruby red precipitate began to form at 0 °C, and continued stirring at 10 °C for 2 h resulted in complete reaction, as the supernatant lightened and no presence of **1a** was detected by FT-IR. The red precipitate was isolated and washed with 5-mL portions of pentane until the washings were clear. The yield was 32.2 mg (67%). IR (CH$_2$Cl$_2$; cm^{-1}): ν(CO) 2022 (s), 1948 (s), 1928 (s), 1714 (m). ^{1}H NMR (360 MHz, CD$_2$Cl$_2$, 23 °C; δ): 8.27 (1H, ddd, $^3J_{P-H}$ = 31.0 Hz, $^3J_{H-H}$ = 9.3 Hz, $^2J_{Rh-H}$ = 0.6 Hz, H$_\alpha$), 5.29 (5H, d, $^2J_{Rh-H}$ = 0.7 Hz, Cp), 4.00 (1H, ddd, $^2J_{P-H}$ = 20.2 Hz, $^3J_{H-H}$ = 9.3 Hz, $^2J_{Rh-H}$ = 2.9 Hz, H$_\beta$), 1.65 (9H, d, $^2J_{P-H}$ = 13.0 Hz, CH$_3$). ^{13}C NMR (90.5 MHz, CD$_2$Cl$_2$, 23 °C; δ): 262.2 (d, $^1J_{Rh-C}$ = 51.0 Hz, bridging CO), 192.8 (CO), 185.5 (CO), 184.2 (CO), 104.8 (dd, $^1J_{Rh-C}$ = 10.1 Hz, $^2J_{P-C}$ = 7.3 Hz, C$_\alpha$), 87.4 (d, $^1J_{Rh-C}$ = 3.8 Hz, Cp), 44.2 (dd, $^1J_{P-C}$ = 82.3 Hz, $^1J_{Rh-C}$ = 20.4 Hz, C$_\beta$), 13.9 (d, $^1J_{P-C}$ = 56.6 Hz, CH$_3$). ^{31}P NMR (162.0 MHz, CD$_2$Cl$_2$, 23 °C; δ): 23.8 (d, $^2J_{Rh-P}$ = 10.8 Hz). Anal. Calcd for C$_{14}$H$_{16}$O$_4$OsPRh: C, 29.38; H, 2.82. Found: C, 29.02; H, 2.62.

(7) For CpRh(CO)(PMe$_3$) $^1J_{Rh-P}$ = 186.0 Hz.[2a] Also see: Verkade, J. G.; Quin, L. D. *^{31}P NMR in Stereochemical Analysis*; VCH: Deerfield Beach, FL, 1987; Chapters 13 and 14.

(8) Crystal data for **4**: C$_{14}$H$_{16}$O$_4$OsPRh, orthorhombic $P2_12_12_1$; a = 8.093(2) Å, b = 16.116(3) Å, c = 12.959(2) Å, V = 1690.2 Å^3, Z = 4, D_{calc} = 2.296 g cm^{-3}. The data were collected at ambient temperature with Mo Kα radiation: μ = 85.895 cm^{-1}, 2θ limits to 50°, 190 variables refined with 3028 unique reflections to R = 0.050 and R_w = 0.060.

dimetallic compounds and used the data to ascertain the amount of carbene character in various types of two-carbon bridges. Most closely related to 4 are a series of metallaphenethylidenes (**D**) prepared by Carty and co-workers.[9b] In complexes such as these, the range of carbon resonances for the α-carbon is from 202.1 to 249.7 ppm, indicating significant carbene character. The β-carbons resonate between 31.0 and 44.9 ppm. This can be compared to the ^{13}C NMR chemical shift values for 4, which are 104.8 and 44.2 ppm for the α- and β-carbons, respectively. The upfield shift of the C_α resonance in 4 is due to its attachment to two metal centers. According to the data collected by Herrmann,[11] the ^{13}C NMR chemical shift range for alkylidene units bridging two metal centers is between 210 and 100 ppm. The C_α resonance for 4 lies inside this range, albeit at the high-field limit. In zwitterionic complexes such as **C**, the range of C_α resonances is from 28.8 to 75.0 ppm, which Carty has attributed to an electron-rich M–M core. Therefore, in reference to Herrmann's parameters, the high-field position of the α-carbon in 4 may then be due to the negative charge on the Os atom.

In conclusion, we have demonstrated that the condensation of **1a** with CpRh(CO)(PR_3) shows a remarkable phosphine dependence. The products obtained are substantially different from the dimetallic species formed from the condensation reaction involving the parent dicarbonyl species. At the present time, the variety of products seen makes it difficult to clarify the role of the phosphine ligand in the reaction into a single, unified mechanism. Several studies are underway to answer this question, and initial results show that the reaction exhibits marked solvent dependence as well. This remarkable product diversity is indicative of the richness of this chemistry, and further work should not only yield answeres but raise additional questions as well.

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Supplementary Material Available: A full structure report for 4, including tables detailing the X-ray data collection and refinement, bond distances, bond angles, torsion angles, least-squares planes, atomic coordinates, and thermal parameters, and a list of spectroscopic data for **3b** (18 pages). Ordering information is given on any current masthead page.

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