Communications

Synthesis, Characterization, and Fluxionality of $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$

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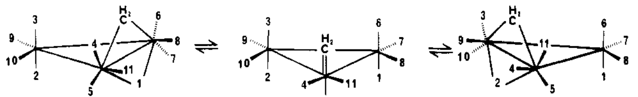
Received December 17, 1984

Summary: The initial product formed in the reaction of $Ru_3(CO)_{12}$ with ethereal CH_2N_2 has been isolated and characterized spectroscopically as $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$. This complex undergoes thermal rearrangement above 45 °C to $H_2Ru_3(CO)_9(CCO)$ and yields the carbon–carbon coupling product $H_2Ru_3(CO)_9(CCH_2)$ on further treatment with CH_2N_2. Spin saturation transfer experiments on $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ indicate that equilibration of the methylene protons occurs near room temperature ($k = 4.0\ s^{-1}$; $\Delta G^{\ddagger} = 17.4$ kcal/mol), apparently via bridge–terminal methylene isomerization.

Surface-bound methylene groups figure predominantly in current mechanistic proposals for reactions of hydrocarbons on metals.[1] We have sought to prepare triruthenium analogues of previously known triosmium methylene complexes.[2,3] We now wish to report the synthesis and characterization of $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ together with its rearrangement to $H_2Ru_3(CO)_9(CCO)$[4] and its coupling reaction with CH_2N_2 to yield $H_2Ru_3(CO)_9(CCH_2)$.[6] We also wish to present NMR evidence supporting facile bridge/terminal interconversion of the methylene group.

Brief (2 min) treatment of $Ru_3(CO)_{12}$ in refluxing cyclohexane with excess ethereal diazomethane (ca. 3 equiv) produces a dark red solution. The reaction is quenched quickly by cooling in an ice bath, and then the solvent and excess CH_2N_2 are removed under vacumm. The residue is extracted with pentane, leaving unreacted $Ru_3(CO)_{12}$ (75% recovery), and $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ is isolated as a red solid (20% conversion) after crystallization at −40 °C. Characterization of the compound as $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ is fully established by IR and ^1H and ^{13}C NMR data.[5] In particular the pattern of ^{13}C NMR signals [1:1:1:2:2:2:2] is in accord with the C_s structure suggested for the analogous $Os_3(CO)_{11}(CH_2)$[2b,c] and found for $Os_3(CO)_{11}(CHSiMe_3)$.[2a,d]

Scheme I



Further reaction of $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ with the excess CH_2N_2 present in solution during its formation yields $H_2Ru_3(CO)_9(CCH_2)$.[6] Treatment of $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ with CH_2N_2 at lower temperatures (down to −30 °C) shows no evidence for the formation of $HRu_3(CO)_{10}(CHCH_2)$, which most likely is the initial coupling product,[2a] so that relatively rapid decarbonylation leads to the observed $H_2Ru_3(CO)_9(CCH_2)$. Note that $Os_3(CO)_{11}(CH_2)$ must be decarbonylated (Me_3NO) before reacting with CH_2N_2[2a] and that the analogous vinyl–vinylidene conversion on the triosmium framework has been observed at a much higher temperature (ca. 130 °C),[7] apparently due to rate-limiting CO loss.

On warming a solution of $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$, rearrangement to $H_2Ru_3(CO)_9(CCO)$[4] is observed ($k = 3.2 \times 10^{-4}\ s^{-1}$ at 47 °C; $\Delta G^{\ddagger} = 25$ kcal/mol). Because the rearrangement is facile at temperatures lower than those required for the synthesis of $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$, extending the reaction time does not lead to more $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ but instead to increased formation of $H_2Ru_3(CO)_9(CCO)$ (up to 50%). The hydrido methylidyne complex $HRu_3(CO)_{10}(CH)$[4] rearranges to $H_2Ru_3(CO)_9(CCO)$ under even milder conditions (ca. −10 °C) and is the probable intermediate in the methylene to carbonylmethylidyne transformation. The analogous osmium transformations, $Os_3(CO)_{11}(CH_2)$ to $HOs_3(CO)_{10}(CH)$[8] to $H_2Os_3(CO)_9(CCO)$,[9] require significantly higher temperatures (≥60 °C) for *both* steps.

The methylene ^1H NMR signals for $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ were observed to broaden on warming a sample to 40 °C, suggesting possible interconversion, but coalescence could not be observed due to the rapid conversion to $H_2Ru_3(CO)_9(CCO)$. ^1H spin saturation transfer experiments indicate that the two methylene protons do in fact exchange ($k = 4.0\ s^{-1}$ at 17 °C; $\Delta G^{\ddagger} = 17.4$ kcal/mol).[10] ^{13}C spin saturation transfer experiments indicate

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[1] (a) Muetterties, E. L.; Stein, J. *Chem Rev.* **1979**, *79*, 479. (b) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159. (c) Osterloh, W. T.; Cornell, M. E.; Pettit, R. *J. Am. Chem. Soc.* **1982**, *104*, 3759.

[2] (a) Shapley, J. R.; Sievert, A. C.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 6975. (b) Steinmetz, G. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 1278. (c) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 825. (d) Churchill; M. R., Wasserman, H. J. *J. Organomet. Chem.* **1983**, *248*, 365.

[3] Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.

[4] Holmgren, J. S.; Shapley, J. R. *Organometallics* **1984**, *3*, 1322.

[5] Anal. Calcd for $Ru_3C_{12}H_2O_{11}$: C, 23.04; H, 0.32. Found: C, 23.00: H, 0.46. Field ionization mass spectrum (^{102}Ru): m/z 628 (M^+). IR (C_6H_{12}): ν_{CO} 2106 (w), 2058 (vs), 2028 (s), 2018 (sh), 2011 (m), 1894 (w) cm^{-1}. IR (KBr) excluding ν_{CO}: 2990 (w), 2942 (w), 1390 (w), 972 (m), 775 (m) cm^{-1}.[5b] ^1H NMR (360 MHz, $CDCl_3$): δ 7.90 (d, $J_{HH} = 5.7$ Hz), 6.02 (d). ^{13}C NMR (90 MHz, $CDCl_3$) of $Ru_3(^*CO)_{11}(CH_2)$ from ca. 50% ^{13}CO-enriched $Ru_3(CO)_{12}$: δ 220.3 (s, 1 C), 206.5 (s, 0.5 C; d, 0.5 C, $^2J_{CC} = 37$ Hz), 205.4 (s, 0.5 C; d, 0.5 C, $^2J_{CC} = 37$ Hz), 195.1 (s, 2 C), 192.6 (s, 2 C), 188.8 (s, 2 C), 186.7 (s, 2 C). ^{13}C NMR (90 MHz, $CDCl_3$) of $Ru_3(CO)_{11}(^*CH_2)$ from ca. 90% ^{13}C enriched CH_2N_2: δ 112.0 (t, $J_{CH} = 144$ Hz). (b) This pattern is identical with that assigned to the bridging methylene group in $Os_3(CO)_{11}(CH_2)$. Oxton, I. A.; Powell, D. B.; Sheppard, N.; Burgess, K.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1982**, 719.

[6] Eady, C. R.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 477. ^{13}C NMR data (261.1 (s, 1 C), 70.5 (t, 1 C, $J_{CH} = 160$ Hz)) unequivocally establishes this as $H_2Ru_3(CO)_9(CCH_2)$, not $H_2Ru_3(CO)_9(HCCH)$. Cf. Evans, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* **1981**, 2017.

[7] (a) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614. (b) Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *85*, C29.

[8] Shapley, J. R.; Cree-Uchiyama, M. E.; St. George, G. M. *J. Am. Chem. Soc.* **1983**, *105*, 140.

[9] Sievert, A. C.; Strickland, D. S.; Shapley, J. R.; Steinmetz, G. R.; Geoffroy, G. L. *Organometallics* **1982**, *1*, 214.

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that irradiation of the bridging carbonyl signal (δ 220.3) causes a strong decrease in intensity of just one other signal, namely, that due to one of the axial sites (δ 206.5). The other axial carbonyl signal (δ 205.4) is unaffected.[11] The activation energy values obtained from the ^1H and ^{13}C spin saturation transfer experiments are in good agreement, indicating that the exchange is due to a single dynamic process. A mechanism derived from that proposed by Cotton for $Fe_3(CO)_{10}(\mu\text{-}CO)_2$[12] is diagrammed in Scheme I. This mechanism is uniquely consistent with exchange of the bridging carbonyl with only one of the axial carbonyls.

Fluxional processes involving bridge-to-terminal alkylidenes have previously been proposed by Knox[13] for $CpRu_2(\mu\text{-}CO)(\mu\text{-}CMe_2)$, Puddephatt[14] for $Co_2(CO)_4(\mu\text{-}CH_2)_2(\mu\text{-}dppm)$, and Bergman[15] for $Cp_2CoRh(CO)_2(\mu\text{-}CH_2)$. This is the first example supporting such a mechanism in a cluster compound.

Further studies on the reactivity of $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ and its derivatives are in progress.

Acknowledgment. We would like to acknowledge the help and advice provided by D. G. Vander Velde in obtaining the spin saturation transfer results. This work was supported by National Science Foundation Grant CHE84-07233. Instruments supported by Grants NSF CHE79-16100 and NIH GM-27029 were utilized for NMR and mass spectra, respectively.

Registry No. $Ru_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$, 95123-28-7; $HzRu_3(CO)_9(CCH_2)$, 55802-24-9; $HzRu_3(CO)_9(CCO)$, 90990-76-4; $Ru_3(CO)_{12}$, 15243-33-1; diazomethane, 334-88-3.

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(10) The ^1H NMR experiments were conducted through selective saturation of the signal at δ 7.90 (site A). The decrease in the intensity of the corresponding signal at δ 6.02 (site B) was then measured. The ^{13}C NMR experiments were conducted by placing the transmitter offset on top of the bridging carbonyl resonance (δ 220.3) and delivering a 30-s, low power pulse. The power of the pulse was attenuated until saturation was obtained. $Ru_3(^*CO)_{12}$ was added to the sample as a standard.

(11) A smaller amount of spin saturation transfer to some of the other carbonyls is also observed. These carbonyls seem to be related to the bridging carbonyl by a secondary process, which is under study.

(12) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4155.

(13) Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 861.

(14) Laws, W. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1020.

(15) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 464.

Oxide-Transfer Reactions within the Monoanionic CO_2 Complex $Li[Fe(\eta\text{-}C_5H_5)(CO)_2(CO_2)]$

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Received January 17, 1985

Summary: Oxide transfer from coordinated CO_2 to coordinated CO is facile above −20 °C in the monoanionic CO_2 complex $Li[Fe(\eta\text{-}C_5H_5)(CO)_2(CO_2)]$. The reaction is proposed to involve intramolecular transfer via a metalloanhydride followed by CO or CO_2 exchange. Oxide transfer to excess CO_2 provides at best a minor decomposition pathway for the CO_2 complex.

The η^1-C coordination mode has been established for one member of the important monoanionic class of transition-metal CO_2 complexes,[1] and a similar metallocarboxylate structure can be inferred for $[Fe(\eta\text{-}C_5H_5)(CO)_2(CO_2)]^-$ ($[Fp(CO_2)]^-$),[2-4] consistent with the nucleophilicity of the CO_2 oxygen atoms.[5,6] Our observation that the reactive oxygen atoms in dianionic η^1-C complexes of CO_2 will transfer to excess CO_2 to give CO_3^{2-} and CO[7,8] and will also transfer from CO_2 to CO ligands[8] has led us to examine the nucleophilicity of the oxygen atoms in $[Fp(CO_2)]^-$. We now wish to report that $[Fp(CO_2)]^-$ transfers oxide between CO_2 and CO ligands but does not reductively disproportionate excess CO_2.[3]

The lithium salt of $[Fp(CO_2)]^-$, prepared by slow addition of CO_2 to a 50 mM solution of Li[Fp][9] at −78 °C, was examined in preference to the equally accessible Na^+ or K^+ salts because of its high solubility and relative stability in tetrahydrofuran (THF).[10,11] This stability is probably a consequence of cation coordination of the carboxylate oxygen atoms,[1,12] the effect of which is illustrated by two reactions: treatment of $NBu_4[Fp]$ with CO_2 at −78 or 25 °C gives a ca. 2:1 mixture of $[Fp]^-$ and $[Fp(CO_2)]^-$, and a similar mixture is obtained when dimethylformamide (DMF) is added to a THF solution of $K[Fp(CO_2)]$ (DMF should inhibit contact ion-pairing by competitively complexing K^+).

Oxide transfer within $Li[Fp(CO_2)]$ was studied by monitoring solutions prepared from equimolar mixtures of $^{13}CO_2$[13] and $C^{18}O_2$.[14] The $Li[Fp(CO_2)]$ was converted into volatile $[FpCH_3]$[15] by quenching 10-mL aliquots with CH_3OSO_2F at −78 °C (eq 1),[16] and mass spectroscopy was

$$Li[Fp(CO_2)] + CH_3OSO_2F \rightarrow [FpCH_3] + LiOSO_2F + CO_2 \quad (1)$$

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† Fellow of the Alfred P. Sloan Foundation, 1982–1985.

(1) (a) Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *100*, 7405. (b) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082.

(2) The $[Fe(\eta\text{-}C_5H_5)(CO)_2]$ moiety will be abbreviated to [Fp] throughout this paper.

(3) Evans, G. O.; Walter, W. F.; Mills, D. R.; Streit, C. A. *J. Organomet. Chem.* **1978**, *144*, C34.

(4) Prepared by direct reaction of CO_2 with Na[Fp][3] or $Mg[Fp]_2$[5]. Phosphine-stabilized derivatives of $[Fp(CO_2)]^-$ have also been prepared from metallocarboxylic acids: Grice, N.; Kao, S. C.; Pettit, R. *J. Am. Chem. Soc.* **1979**, *101*, 1627.

(5) Forschner, T.; Menard, K.; Cutler, A. *J. Chem. Soc., Chem. Commun.* **1984**, 121.

(6) Bodner, T.; Coman, E.; Menard, K.; Cutler, A. *Inorg. Chem.* **1982**, *21*, 1275.

(7) Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1980**, *102*, 7604.

(8) Maher, J. M.; Lee, G. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 6797.

(9) Wong, A.; Harris, M.; Atwood, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 4529.

(10) The 1:1 adduct stoichiometry has been confirmed to within 5% by gas titration using vacuum line techniques for the Li^+, Na^+, and K^+ salts of $[Fp(CO_2)]^-$. There is no evidence for the formation of a subsequent 2:1 CO_2 adduct with Li, Na, or KFp: the carbonyl stretching absorptions of the corresponding $[Fp(CO_2)]^-$ salts and the CO_2 stretching absorption of $Li[Fp(CO_2)]$ (the only salt for which such an absorption can be observed[12]) are unaffected by excess CO_2.

(11) The counterion dependence of stability and solubility parallel each other and vary as $Li^+ > Na^+ > K^+ > NBu_4^+$.

(12) Specific coordination of M^+ to the carboxylate group is indicated by the absence of counterion dependence for the carbonyl stretching absorptions (at 2015 and 1950 cm^{-1} for Li^+, Na^+, K^+, and NBu_4^+ salts), together with the counterion sensitivity of the C–O stretching absorption of the coordinated CO_2. Although partially obscured by solvent, this is at 1510 cm^{-1} in $Li[Fp(CO_2)]$ (ca. 1480 cm^{-1} in $Li[Fp(^{13}CO_2)]$) but is below the solvent cutoff (ca. 1450 cm^{-1}) in THF solutions of $Na[Fp(CO_2)]$, $K[Fp(CO_2)]$, and $NBu_4[Fp(CO_2)]$.

(13) Merck, Sharpe and Dohme: 92.97 atom % ^{13}C.

(14) Prochem: 99.39 atom % ^{18}O.

(15) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

(16) This reaction is similar to that reported between $Na[Fp(CO_2)]$ and MeI,[3] but solution IR indicated that the reaction was clean and complete in less than 5 min at −78 °C with $MeOSO_2F$, while more vigorous conditions (>−40 °C), under which scrambling occurred, were required for reaction with MeI.

0276-7333/85/2304-0794$01.50/0