The reaction of $(\mu\text{-H})_2Os_3(CO)_9(PPh_3)$ with ethylene affords the ethylidene complex $(\mu\text{-H})_2Os_3(CO)_9(PPh_3)(\mu\text{-CHCH}_3)$

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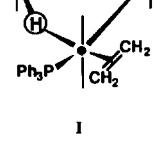
Abstract

The product isolated from the reaction of $(\mu\text{-H})_2Os_3(CO)_9(PPh_3)$ with ethylene is shown to be the ethylidene complex $(\mu\text{-H})_2Os_3(CO)_9(PPh_3)(\mu\text{-CHCH}_3)$ (1) rather than the ethylene complex $(\mu\text{-H})(H)Os_3(CO)_9(PPh_3)(C_2H_4)$, as previously claimed. The characterization of 1 is based on a combination of ^1H and ^{13}C NMR results. The ^1H NMR data (δ 6.84 (1 H_D), 2.53 (3 H_C), $J(CD) = 7.4$ Hz) establish the presence of the ethylidene moiety, whereas detailed analysis of the 1-D and 2-D ^{13}C NMR spectra of ^{13}CO-enriched 1 indicates the relative positions of the ethylidene, hydride, and phosphine ligands on the triosmium framework.

Key words: Osmium; alkylidene; Hydride; Carbon-13; Cluster; Nuclear magnetic resonance

1. Introduction

The reaction of $(\mu\text{-H})_2Os_3(CO)_9(PPh_3)$ with ethylene was claimed to form an ethylene adduct $(\mu\text{-H})(H)Os_3(CO)_9(PPh_3)(C_2H_4)$ (see I), on the basis of spectroscopic data [1]. An intermediate complex was not observed in the analogous reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ with ethylene [2–4]; the ethyl complex $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CH}_2CH_3)$ and its tautomer, the ethylidene complex $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CHCH}_3)$ were the first species seen [5]. We have re-examined the reaction of $(\mu\text{-H})_2Os_3(CO)_9(PPh_3)$ with ethylene, and the results described here show that the ethylene complex originally claimed is actually the ethylidene species $(\mu\text{-H})_2Os_3(CO)_9(PPh_3)(\mu\text{-CHCH}_3)$ (1) (see II).



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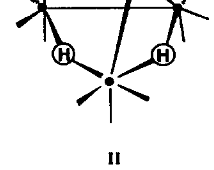

II

2. Results

The reaction of $(\mu\text{-H})_2Os_3(CO)_9(PPh_3)$ with ethylene (60 psig) at room temperature overnight gave the same complex 1 as previously reported [1], on the basis of its IR, ^1H NMR, and mass spectral data. This compound slowly decomposes in solution, and repeated attempts to obtain crystals suitable for X-ray diffraction have been unsuccessful.

2.1. ^1H NMR studies

The ^1H NMR spectrum of 1 in acetone-d_6 at −30°C displays a multiplet at δ 7.0–7.5 assigned to the phenyl protons in the PPh_3 ligand, a doublet at δ 2.53, and two resonances in the high field region due to hydride ligands, all of which have been previously reported [1]. However, we observe another resonance; a quartet of multiplets at δ 6.84. ^1H homonuclear decoupling experiments (see Fig. 1) confirm that the resonance at δ 6.84 is a part of the spin system in compound 1. In particular, upon irradiation of this multiplet, the doublet at δ 2.53 collapses into a singlet. This result clearly shows the splitting of 7.4 Hz observed in the resonance at δ 2.53 is caused by the methine proton at δ 6.84 rather than by coupling to the phosphorus nucleus in the phosphine ligand as had been proposed

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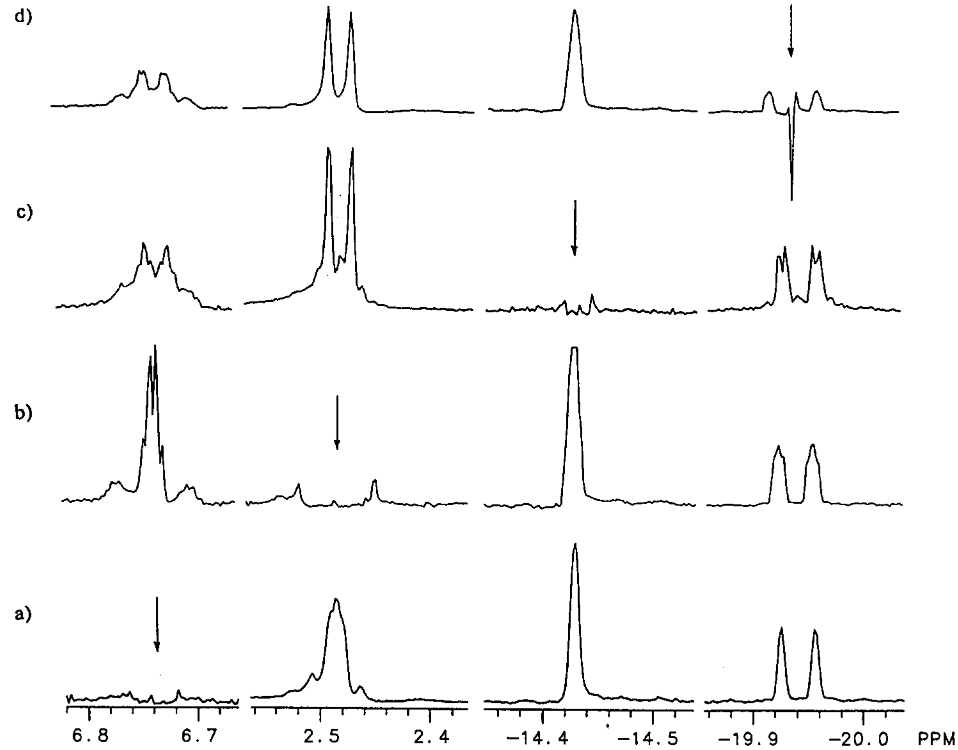


Fig. 1. Selective decoupling of the ^1H NMR spectrum of $(\mu\text{-}H)_2Os_3(CO)_9(PPh_3)(\mu\text{-}CHCH_3)$ in acetone-d_6 at −30°C: (a) resonance at D irradiated; (b) resonance at C irradiated; (c) resonance A irradiated; (d) resonance B irradiated. See Table 1 for specific assignments.

previously [1]. Therefore, this complex does not contain an ethylene ligand, but rather an ethylidene CH_3CH moiety. The coupling constants along with other ^1H NMR parameters are summarized in Table 1.

2.2. ^{13}C NMR studies

^1H broad-band decoupled ^{13}C-NMR spectra of ^{13}CO-enriched (1*) at −40°C in acetone-d_6 display nine carbonyl resonances, each of which has the same signal intensity (Fig. 2(a)). From high to low field they are designated as 1 to 9. Under these circumstances resonances 8 and 9 appear as triplets of doublets. The triplet pattern is readily recognized as due to a singlet overlapped with a pair of satellite peaks caused by partial ^{13}C incorporation (*ca.* 50%) and a large two-bond coupling of 33 Hz for a pair of *trans* axial carbonyl ligands. The further doublet splitting is due to phosphorus coupling of 4.7 Hz. This suggests, and further discussion will confirm, that the phosphine ligand is in an equatorial position on the osmium atom with the trans, diaxial carbonyls, *i.e.*, this forms an $Os(CO)_3PPh_3$ unit.

^1H selectively decoupled ^{13}C-NMR spectra of 1* in CD_2Cl_2 at −40°C were obtained for the assignment of the carbonyl resonances (Fig. 2). Four spectra were recorded under identical conditions except for the de-

TABLE 1. Comparison of ^1H NMR parameters for $(\mu\text{-}H)_2Os_3(CO)_9(PPh_3)(\mu\text{-}CHCH_3)$ and $(\mu\text{-}H)_2Os_3(CO)_{10}(\mu\text{-}CHCH_3)$

$(\mu\text{-}H)_2Os_3(CO)_9(PPh_3)(\mu\text{-}CHCH_3)$ [a]			$(\mu\text{-}H)_2Os_3(CO)_{10}(\mu\text{-}CHCH_3)$ [b]			Assignment
δ	mult [c]	int	δ	mult [d]	int	
7.0–7.5	m	15H				C_6H_5
6.84	qm	1H	6.76	q	1H	CH(D)
2.53	d	3H	2.49	d	3H	CH_3(C)
−14.27	d	1H	−14.26	s	1H	Os–H–Os(A)
−19.82	dt	1H	−20.34	s	1H	Os–H–Os(B)

[a] At −30°C; acetone-d_6. [b] At −10°C in CD_2Cl_2 [5]. [c] J(BD) = 2.0 Hz, J(AD) = 2.0 Hz, J(AB) = 1Hz, J(CD) = 7.4 Hz, J(PB) = 11.0 Hz, J(PD) = 2.0Hz. [d] J(CD) = 7 Hz.

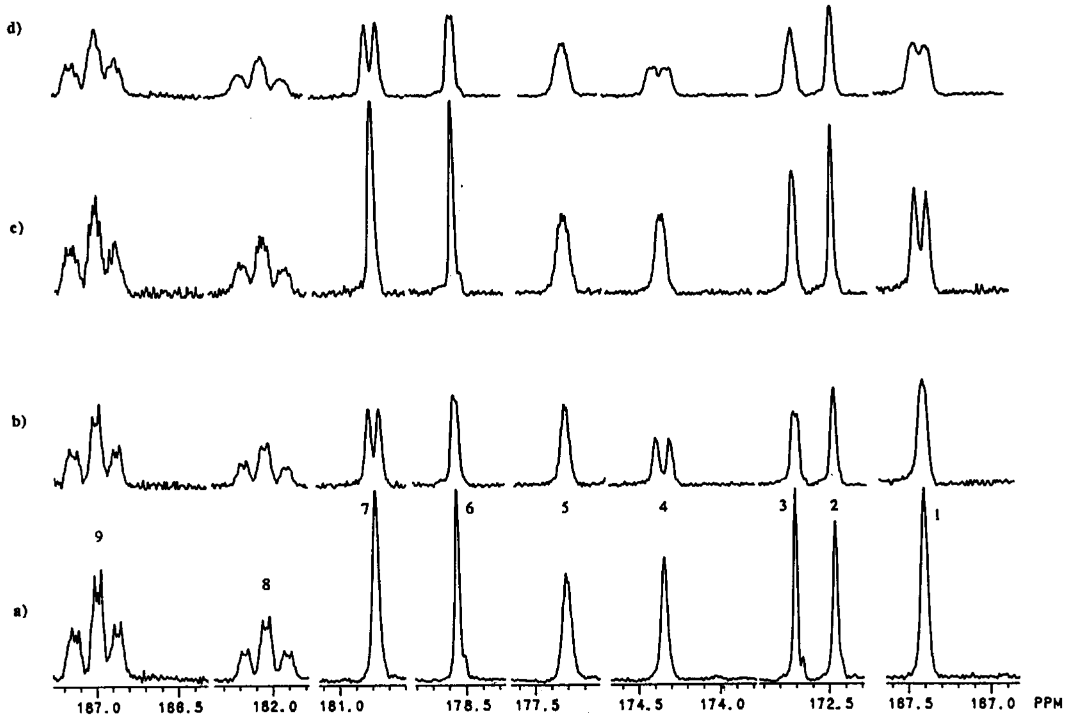


Fig. 2. Carbonyl region ^{13}C NMR spectra of $(\mu\text{-H})_2Os_3(CO)_9(PPh_3)(\mu\text{-CHCH}_3)$ in CD_2Cl_2 at −40°C: (a) ^1H decoupled; (b) H_B selectively decoupled; (c) H_A selectively decoupled; (d) ^1H coupled.

coupling status: one ^1H broad-band decoupled spectrum, one ^1H coupled spectrum, and two selectively ^1H decoupled spectra irradiating either H_A or H_B. Coupling constants between the carbonyl carbons and the hydride ligands are summarized in Table 2.

TABLE 2. ^{13}C NMR parameters for $(\mu\text{-H})_2Os_3(CO)_9(PPh_3)(\mu\text{-CHCH}_3)$ [a]

Peak	Chemical shift [b]	Coupling constants (Hz) [d]			
		C-H$_A$	C-H$_B$	C-C [c]	C-P [c]
1	167.4	w	9.2	3.4	
2	172.5	w	–	3.3	1.1
3	172.7	2.9	w	w	w
4	174.3	10.8	2.4	3.5	
5	177.3	–	w	w	*ca.* 4–5
6	178.6	2.2	–	w	
7	180.8	7.9	–	w	
8	182.0	–	*ca.* 2–3	*ca.* 4–5 32.9 (trans)	5.1
9	187.0	–	*ca.* 2–3	4.7 33.1 (trans)	5.3

[a] The spectra were recorded at 125.76 MHz in CD_2Cl_2 at 233 K unless noted otherwise. [b] Chemical shifts (ppm) were referenced to the methylene carbon in CD_2Cl_2 as δ 53.8. [c] Based on ^1H-decoupled spectra recorded at 75.48 MHz in acetone-d_6 at 243 K with resolution enhancement (see Fig. 4 and Experimental section). [d] The entry w indicates observation of a small, but unresolved coupling.

The unsymmetrized $^{13}C\{^1H\}$COSY spectrum of 1* in CD_2Cl_2 at −40°C is shown in Fig. 3. Upon resolution enhanced apodization, some resonances exhibit

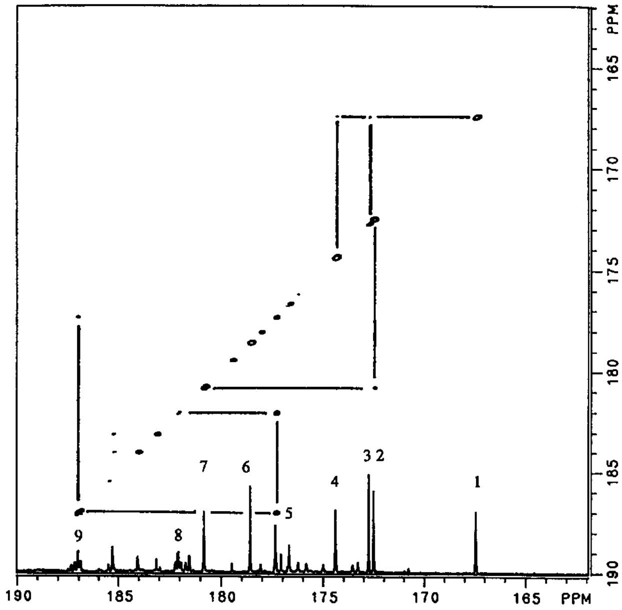


Fig. 3. Unsymmetrized $^{13}C\{^1H\}$ COSY spectrum of $(\mu\text{-H})_2Os_3(CO)_9(PPh_3)(\mu\text{-CHCH}_3)$ in CD_2Cl_2 at −40°C. Minor peaks are due to residual $(\mu\text{-H})_2Os_3(CO)_9(PPh_3)$.

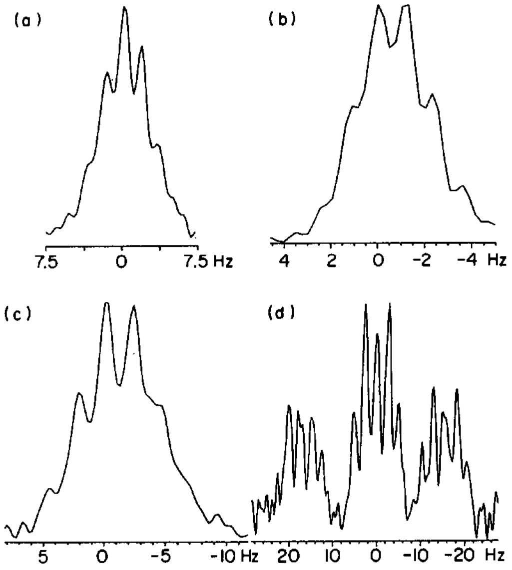
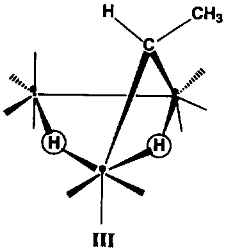


Fig. 4. Expansion of four carbonyl carbon resonances of $(\mu\text{-}H)_2Os_3(CO)_9(PPh_3)(\mu\text{-}CHCH_3)$ in CD_2Cl_2 at −40°C: (a) resonance 1; (b) resonance 2; (c) resonance 5; (d) resonance 9.

intricate multiplicities as displayed in Fig. 4. The derived ^{13}C NMR parameters are also summarized in Table 2.

3. Discussion

As shown in Table 1, the ^1H chemical shifts of the methyl, the methine, and the two hydride resonances in **1** are all very similar to those of the closely related ethylidene complex, $(\mu\text{-}H)_2Os_3(CO)_{10}(\mu\text{-}CHCH_3)$ [5]. The configuration of the latter compound (see **III**) was deduced by comparison of spectroscopic properties with those of $(\mu\text{-}H)_2Os_3(CO)_{10}(\mu\text{-}CH_2)$, the structure of which (see **IV**) has been determined by both X-ray and neutron diffraction studies [6–8]. The position of the phosphine ligand, however, is not clear from the ^1H NMR data alone, so the ^{13}C NMR spectrum of **1*** (* denotes ^{13}CO enrichment) has been studied by several techniques.



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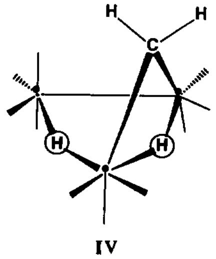
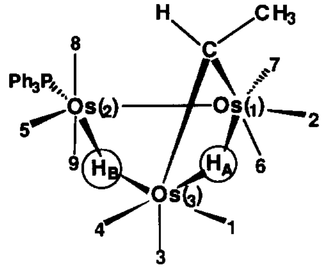


IV

3.1. Selective proton decoupling

Analysis of the selective decoupling experiments shown in Fig. 2 and summarized in Table 2 indicates that a three-bond coupling between a carbonyl carbon and bridging hydride is undetectable, whereas every two-bond coupling is visible [10–13]. Each carbonyl resonance can be classified into one of three sets: coupled only to H_A, coupled only to H_B, and coupled to both H_A and H_B. Each set of resonances therefore corresponds to the carbonyls coordinated to a particular osmium atom, according to the labeling shown in **V**.



V

Since resonances 2, 6 and 7 are coupled only to H_A, the Os(1) center is coordinated by the three corresponding carbonyl ligands. Due to the relatively large $^2J(CH)$ coupling of 7.9 Hz, resonance 7 is assigned to the pseudoaxial carbonyl trans to H_A [10–18]. Given its similarly downfield position [19–21], resonance 6 is assigned to the carbonyl in the other pseudo-axial position. This leaves resonance 2 for the carbonyl in the equatorial position *trans* to the unbridged metal–metal bond.

Since resonances 5, 8, and 9 are coupled only to H_B, the three corresponding carbonyls are associated with Os(2). Resonances 8 and 9 are readily assigned to the pair of *trans* axial carbonyls, due to the large two-bond coupling [5,26–29]. Specific structural assignment of these signals individually is not unambiguous; however, in analogy to the situation for $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CH)$ [21], the upfield resonance 8 is assigned to the axial carbonyl located in the same side of the triosmium plane as the ethylidene ligand, whereas the downfield resonance 9 is attributed to the other axial carbonyl. Resonance 5 shows a small coupling to H_B and a relatively large coupling to the phosphorus nucleus. Therefore, resonance 5 is assigned to the equatorial carbonyl in a *cis* position to H_B, and the position *trans* to H_B is occupied by the phosphine ligand.

Resonances 1, 3, and 4 are coupled to both H_A and H_B; thus, the corresponding carbonyls are bonded to Os(3). Since resonances 1 and 4 show strong couplings to H_B and H_A, respectively, they are assigned to the corresponding carbonyls *trans* to H_B and H_A [15–18]. This leaves resonance 3 to be assigned to the pseudo-axial position on the same metal center.

3.2. Carbon–carbon COSY

The ^{13}C COSY spectra of ^{13}CO-enriched triosmium carbonyl, clusters have shown that only two-bond couplings appear in the cross peaks, that is, two resonances that generate an off-diagonal peak correspond to two carbonyl ligands at the same osmium atom [22,23*]. In the ^{13}C COSY spectrum of **1***, both resonances 8 and 9 show cross peaks with resonance 5. Therefore, since resonances 8 and 9 are assigned to the *trans* axial carbonyls, resonance 5 is assigned to an equatorial carbonyl on the same metal center. Furthermore, resonance 1 is coupled to both resonances 3 and 4; thus, one osmium center contains at least the three corresponding carbonyl ligands. Finally, resonance 2 shows off-diagonal peaks with resonance 7, and therefore the third osmium center bears at least these two carbonyl ligands.

Couplings of resonance 6 to resonances 2 and 7, which correspond to the other two carbonyls in the same $Os(CO)_3$, unit, were not detected in the ^{13}C COSY experiments. Resonances 8 and 9 also did not show any cross peak in the ^{13}C COSY spectra. These absences are not likely due to strongly different T_1 (or T_2) values; however the data acquisition parameters were not separately optimized for strongly different values of $^2J(CC)$ [24*,25*].

3.3. High resolution multiplicity analysis

Upon resolution enhanced apodization, some of the carbonyl resonances exhibit intricate multiplicities (Fig. 4). Resonances 8 and 9 appear to be triplets of doublets of triplets. The apparent triplet with the larger coupling constant in either resonance 8 or 9 is a singlet with a pair of satellite peaks caused by partial ^{13}C incorporation (*ca.* 50%) in the *trans* axial carbonyl ligands, which have a large two-bond coupling constant of 33 Hz [5,26–29]. The doublet splitting is due to phosphorus coupling of *ca.* 5 Hz, a typical value for $^2J(PC)_{cis}$ [10,11,20,30–33]. Finally, the smaller apparent triplet is due to overlap of a singlet with a doublet resulting from $^2J(CC)_{cis} = 4–5$ Hz. Thus, this detailed analysis of either resonance 8 or 9, assigned to one of the axial carbonyls, reveals the presence of the other axial carbonyl, a phosphine ligand in a *cis* position, and another carbonyl in the remaining *cis* position.

In a similar fashion, the apparent quintet shown by either resonance 1 or 4 is seen to be a singlet superimposed by both a doublet and a triplet caused by statistical ^{13}CO incorporation in an $Os(CO)_3$ unit. Two ^{12}CO ligands in the other two sites make a singlet, one ^{13}CO and one ^{12}CO make a doublet, and two ^{13}CO ligands make a triplet; the overlap of the singlet, the doublet and the triplet gives a quintet [23]. The $^2J(CC)_{cis}$ coupling of *ca.* 3.5 Hz is consistent with the coupling found in $(\mu\text{-H})_2Os_3(CO)_{10}$ [23]. Thus, either resonance 1 or 4 corresponds to a carbonyl ligand in an $Os(CO)_3$ unit; from this data alone the two ligands do not necessarily belong to the same $Os(CO)_3$ unit although they actually do.

The apparent quintet observed in resonance 2 indicates that it also corresponds to an osmium carbonyl unit containing exactly three carbonyl ligands. This result agrees with the conclusions from ^{13}C COSY and ^{1}H selective decoupling. Resonance 2 also shows a $^3J(PC)$ coupling of 1.1 Hz. Among the three carbonyl carbons on the Os(1) unit, the best candidate for significant phosphorus coupling is the carbonyl *trans* to the unbridged metal–metal bond [10,13,33]. This agrees with and confirms the previous assignment.

3.4. Comparison of approaches

In a COSY experiment the detection of homonuclear couplings is facilitated by spreading information on magnetization to two dimensions, but this occurs with a considerable loss of resolution. In contrast, the detailed multiplicity analysis requires high-resolution one-dimensional spectra that necessarily sacrifice the signal to noise ratio.

In this study of **1***, ^{13}C COSY gives a direct correlation of two coupled signals while the multiplicity analysis does not. Moreover, sometimes the line shape of a resonance is obscured by the overlap of so many couplings that no meaningful information is obtained. Nevertheless, the two experiments are complementary. ^{13}C COSY data gives only the minimum number of carbonyls that coordinate to the same osmium center because one or more carbonyls may remain undetected. On the other hand, the detailed analysis of the multiplicity of one carbonyl resonance can reveal exactly how many carbonyl ligands are bound to that particular osmium atom.

Selective ^{1}H decoupling experiments can show whether a carbonyl is bound to the same metal atom as a particular hydride ligand and whether there is a *cis* or *trans* relationship. In the particular case that a triangular carbonyl cluster contains two inequivalent hydrides bridging separate edges, such as **1**, these selective decoupling experiments allow more individual signal assignments than the ^{13}C COSY experiments.

3.5. Formation of 1

At room temperature in solution the ethylidene complex $(\mu\text{-H})_2Os_3\text{-}(CO)_{10}(\mu\text{-CHCH}_3)$ exists in equilibrium with its ethyl tautomer $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CH}_2CH_3)$ in the ratio of 7:1 [5]. Although we found no evidence in the NMR spectra of **1** for the corresponding ethyl complex, it is likely that such a species

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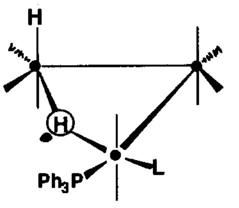
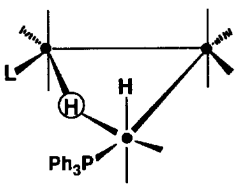
* Reference number with asterisk indicates a note in the list of references.

is involved in both the formation and decomposition of **1**.

The formation of only one structural isomer of **1** is notable, although similar structural specificity has been observed in the reaction of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{PPh}_3)$ with 2,3-dihydrothiophene [34] as well as in several related reactions of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{PPhMe}_2)$ with unsaturated substrates [35]. The reaction of acetylene with $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{PPh}_3)$, in contrast, gives two isomeric insertion products [1,36]. At least two products from such insertion reactions with $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{PPh}_3)$ might be expected, since the incoming ligand could form an initial adduct at either the phosphine-substituted osmium center or at the unsubstituted center (see **VI** and **VII**). In the specific case of L = ethylene it would appear that only **VII** is involved in forming **1**. In this case, as well as in most cases involving unsaturated organic reactants, it is likely that **VI** is destabilized by steric interactions between the incoming group and the triphenylphosphine ligand.



VI



VII

4. Experimental section

4.1. General

All manipulations were performed under a N_2 atmosphere using standard Schlenk techniques: n-Hexane (American Burdick & Jackson) was treated with sulfuric acid and then distilled over sodium-potassium alloy prior to use. $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{PPh}_3)$ was prepared by a literature method [14]. ^{13}CO (99%) was purchased from Isotec and used without further purification. ^{13}CO enrichment (*ca.* 50%) of $\text{Os}_3(\text{CO})_{12}$ was achieved by heating for 3 days at 120°C in decalin in the presence of 12 equiv. of ^{13}CO in a pressure bottle. Infrared spectra were recorded on a Perkin-Elmer 1750 FT-IR spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois. Field desorption mass spectra were obtained on a Varian-MAT 731 mass spectrometer by the Mass Spectrometry Laboratory of the School of Chemical Sciences.

4.2. Preparation of $(\mu\text{-}H)_2Os_3(CO)_9(PPh_3)(\mu\text{-}CHCH_3)$

A solution of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9\text{-}(\text{PPh}_3)$ (41.2 mg) in n-hexane (60 ml) was stirred in a pressure bottle (250 ml) under C_2H_4 (60 psig) for 15 h. After venting the bottle, the solvent was reduced to a small volume under vacuum at 0°C. The solution was cooled to -78°C to precipitate yellow solid **1** (39.4 mg, 93%) Anal. Found; C, 31.59; H, 2.48; P, 2.78. $\text{C}_{29}\text{H}_{21}\text{O}_9\text{Os}_3\text{P}$ calcd.:C, 31.24; H, 1.90; P, 2.78%. MS (field desorption; ^{192}Os): m/z 1120 (M^+); 1092 $[\text{M}-\text{C}_2\text{H}_4$ or $\text{M}-\text{CO}]^+$ IR (cyclohexane): $\nu(\text{CO})$ 2090 w, 2069 m, 2042 m, 2006 vs, 2000 m, 1988 sh,w, 1971 w, 1965 w cm^{-1}.

4.3. NMR spectroscopy

^1H NMR spectra of **1** in acetone-d_6 at -30°C were recorded at 360.057 MHz on a Nicolet NT-360 spectrometer with a 1180 computer and a 293B pulse programmer. ^1H chemical shifts were referenced to the residual proton signal in the solvent at δ 2.04.

High-resolution ^1H broad-band decoupled ^{13}C-NMR spectra of **1*** in acetone-d_6 at -30°C were recorded at 75.48 MHz with 32 K data points on a General Electric QE-300 spectrometer. The FID thus obtained underwent zero-filling twice into a 128 K data set; digital resolution of 0.26 Hz was achieved. No apodization was applied. The decoupling frequency for ^1H broad-band decoupling was adjusted to center at δ 15 in order to ensure decoupling of the high-field hydride region.

^1H selective decoupled ^{13}C NMR experiments of **1*** in CD_2Cl_2 were recorded at 125.76 MHz at -40°C on a General Electric GN-500 spectrometer equipped with an NIC 1280 computer. All T_1 experiments were performed with the fast inversion-recovery sequence, a symmetric five-element composite 180° pulse, alternating phase of the 90° pulse, and a nonlinear three-parameter least squares fit. Reported ^{13}C chemical shifts were referenced to the methylene carbon resonance of CD_2Cl_2 at δ 53.8.

A $^{13}\text{C}\{^1\text{H}\}$ COSY experiment of **1*** in CD_2Cl_2 was recorded on a General Electric GN-500 spectrometer at -40°C using a COSY pulse sequence with additional delays of 50 ms. The data matrix was acquired with 512 data points in t_1 and 1024 data points in t_2. A total of 64 1-D spectra along the t_1 dimension were collected. Apodization was applied to all data sets with 10° shifted sine bell. In the final spectrum, frequency domain matrices were not symmetrized along the $F_1 = F_2$ diagonal, since it turned out that symmetrization caused the disappearance of a few genuine cross peaks.

Acknowledgments

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