is stable in dry air for several days.

The accurate stoichiometry and structure of **2** were determined by single-crystal X-ray diffraction analysis.[10] The compound crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. Crystal data are as follows: a = 15.851 (4) Å, b = 15.496 (4) Å, c = 23.061 (3) Å; β = 93.80 (2)°; V = 5652.0 (2) Å^3; ρ_{calcd} = 1.89 g cm^{-3}; μ(Mo Kα) = 43.2 cm^{-1}; $F(000)$ = 3200; R_F = 0.065 and R_{wF} = 0.067 for 7116 unique reflections with $F^2 \geq 3\sigma(F^2)$.[12] A view of the molecular structure of **2** is shown in Figure 1, an atom-labeling scheme is shown in Figure 2, and averaged intramolecular bond distances and angles are presented in Table I.[12]

The X-ray analysis clearly reveals that **2** contains a central uranium atom surrounded by four **1**$^-$ ligands, and each ligand is bonded to the uranium atom in a bidentate fashion through the phosphoryl oxygen atoms. The eight phosphoryl oxygen atoms form a square antiprism which closely resembles the coordination polyhedron found for U(acac)$_4$.[13] The U–O(phosphoryl) distances range from 2.346 (9) to 2.381 (10) Å (average 2.355 Å). These distances are similar to the U–O(phosphoryl) distance reported for $UO_2(NO_3)_2(Bu_3PO)_2$, 2.347 (6) Å,[14] and shorter than the U–O(phosphoryl) distance found for $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2]$, 2.420 (4) Å.[15] The U–O(phosphoryl) distances also are similar to the U–O(carbonyl) distances in U(acac)$_4$, 2.23 (3)–2.37 (4) Å.[13] The long U···Ni separations (average 4.750 (2) Å) indicate that there is no significant interaction between these metal atoms. The accompanying U—O═P angles in the inner coordination sphere range from 148.9 (6) to 152.0 (6)° (average 150.1 (6)°). The individual oxygen atom–oxygen atom "bite" distances range from 2.74 (1) to 2.82 (1) Å (average 2.79 Å), and the remaining O–O edge distances on the polyhedron range from 2.75 (1) to 3.33 (1) Å (average 2.93 Å).

The structural features of the coordinated anion **1**$^-$ also are of interest. The phosphoryl P═O bond distances range from 1.49 (1) to 1.52 (1) Å (average 1.51 (1) Å), and these distances are on the long end of the bond distance range usually associated with metal-coordinated phosphoryl groups.[8,16] The P–OCH$_3$ bond distances range from 1.59 (1) to 1.63 (1) Å (average 1.61 (1) Å),[17] and these distances also are on the long end of P–OR bond distances found in many complexes containing (RO)$_2$(X)P═O—M units.[16] The average bond angles in this unit are as expected: Ni—P═O = 121.7 (4)°, Ni—P—O = 109.6 (5)°, and P—O—C = 121.1 (12)°.

The Ni–P bond distances range from 2.116 (4) to 2.139 (4) Å (average 2.126 (4) Å). Few comparative data are available for similar bonding arrangements; however, the distances are comparable to a number of Ni–P distances for classical nickel phosphite coordination compounds.[16] The Ni–C atom bond distances associated with the Ni–Cp interaction average 2.12 (2) Å, and these distances are similar to distances reported for a number of CpNi(PPh$_3$)R complexes.[18]

Lukehart has previously suggested that the combination of UCp$_2$(NEt$_2$)$_2$ and the rhena β-diketone {Re(CO)$_4$[C(O)CH$_3$]$_2$}H leads to the formation of a trinuclear complex Cp$_2$U{Re(CO)$_4$[C(O)CH$_3$]$_2$}$_2$ (**3**); however, a full description of this complex has not appeared. The synthesis and structure determination of **2** supports the comparison mentioned above between the metalla β-diketonate and metalla β-diphosphonate ligands and indirectly offers some credence to the proposed composition of the trinuclear complex **3**. In addition, **2** represents the first example of a complex containing a metalla β-diphosphonate ligand bonded to an actinide element, and the first structurally characterized example of a mixed transition metal–actinide coordination complex.[19] Additional studies of the coordination properties of **1**$^-$ with organo actinide and lanthanide fragments are in progress.

Acknowledgment. R.T.P. wishes to acknowledge the Department of Energy, Office of Basic Energy Sciences, Grant No. 79ER-10465, for partial support of this work. We also wish to acknowledge an NSF Grant CHE-7802921 which facilitated the purchase of the X-ray diffractometer at UNM. We also wish to acknowledge helpful discussions with Professor J. Gilje, University of Hawaii.

Registry No. 2, 82150-24-1; {Ni[P(O)(OCH$_3$)$_2$]$_2$(η^5-C$_5$H$_5$)$^-$}[NH$_4^+$], 62126-01-6; UCl$_4$, 10026-10-5.

Supplementary Material Available: A full description of the data collection and structure solution and tables of observed and calculated structure factors, atomic positional parameters, thermal parameters, and bond angles and distances (30 pages). Ordering information is given on any current masthead page.

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(9) Yield: 85%; IR (mull) 1089, 1040, 1005, 835, 797, 762, 720, 623, 590 cm^{-1}. Satisfactory NMR data were not obtained primarily because of the low solubility of **2** in common organic solvents. Single crystals were obtained by slow evaporation of a THF solution of **2**.

(10) X-ray data were collected with a Syntex P3/F automated four-circle diffractometer (Mo Kα radiation, $\bar{\lambda}$ = 0.71069 Å), and the structure was solved with the Syntex XTL system. A full description of the data collection and structure solution is available in the supplementary material.[11]

(11) Supplementary material.

(12) Tables of observed and calculated structure factors, atomic positional parameters, and thermal parameters and a full listing of bond angles and distances are available.[11]

(13) Titze, H. *Acta Chem. Scand.* **1970**, *24*, 405.

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(17) The P(1)–O(3) bond distance is unusually long, 1.69 Å, and the thermal parameters of O(3) are large. A difference map showed another peak close to O(3), and a disorder of O(3) over two sites was indicated.[11] Only one position was found for the attached C(2) atom, and the P(1)–O(3) bond distance was not included in the average bond distance range listed in the text.

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(19) The first structural characterization of a bimetallic transition metal–lanthanide coordination complex, (Me$_5$C$_5$)$_2$Yb–(THF)Co(CO)$_4$ was recently reported: Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* 1981, 985.

Alkylation of Transition Metal Alkoxides and Aryl Oxides

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Summary: Treatment of transition metal alkoxides and aryl oxides with lithium alkyls gives rise to varying amounts of substitution depending on the metal, alkyl, alkoxide (or aryl oxide) and solvent.

There are numerous examples in the literature of transition metal alkoxides being used as substrates for the synthesis of alkyl compounds.[1] Alkoxides can offer nu-

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Table I

$M(OR)_5$[c]	LiR'	product[a,b]
$Ta(OMe)_5$	$LiCH_2SiMe_3$	$Ta(OMe)(CH_2SiMe_3)_4$ (**3**)
$Ta(OMe)_5$	$LiCH_2CMe_3$	$Ta(OMe)_2(CH_2CMe_3)_3$ (**4**)
$Ta(O\text{-}i\text{-}Pr)_5$	$LiCH_3$	$Ta(O\text{-}i\text{-}Pr)_2(CH_3)_3$ (**5**)
$M(O\text{-}i\text{-}Pr)_5$	$LiCH_2SiMe_3$	$M(O\text{-}i\text{-}Pr)_2(CH_2SiMe_3)_3$ (**6a,b**)
$Ta(OC_6H_3Me_2)_5$[11]	$LiCH_2SiMe_3$	$Ta(OC_6H_3Me_2)_2(CH_2CMe_3)_3$ (**7**)
$M(OC_6H_3Me_2)_5$	$LiCH_2SiMe_3$	$M(OC_6H_3Me_2)_2(CH_2SiMe_3)_3$ (**8**)
$Ta(OC_6H_3\text{-}t\text{-}Bu_2)_2Cl_3$[12]	$LiCH_3$	$Ta(OC_6H_3\text{-}t\text{-}Bu_2)_2(CH_3)_3$ (**9**)
$Ta(OC_6H_3\text{-}t\text{-}Bu_2)_2Cl_3$	$LiCH_2SiMe_3$	$Ta(OC_6H_3\text{-}t\text{-}Bu_2)_2(CHSiMe_3)(CH_2SiMe_3)$ (**10**)

[a] Satisfactory elemental analysis were obtained for all new compounds. ^1H NMR data are collected.[16] [b] All of the compounds gave mass spectra, the strongest peaks being due to $(M - OR)^+$ and $(M - R')^+$. [c] $OC_6H_3Me_2$ = $OC_6H_3Me_2$ = 2,6-dimethylphenoxide; $OC_6H_3\text{-}t\text{-}Bu_2$ = 2,6-di-*tert*-butylphenoxide.

merous advantages over halide starting materials such as their more discrete nature especially for metals in lower oxidation states.[2] However, no systematic study of the utility of this reaction has been reported. We communicate here some of our initial studies of this reaction.

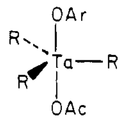
The alkylation of $[MoCl_3]_n$ with $LiCH_2SiMe_3$ leads to the dinuclear compound $Mo_2(CH_2SiMe_3)_6$ (Mo≡Mo) (**1**) in no more than 25% yield.[3] We find that by using the dinuclear alkoxides $Mo_2(O\text{-}i\text{-}Pr)_6$[4] and carrying out the reaction in pentane, yields as high as 75% can be obtained.[5] Addition of a deficit of $LiCH_2SiMe_3$ (4 equiv) gave rise to an inseparable mixture, the only components of which that could be identified by ^1H NMR being **1** and 1,2-$Mo_2(O\text{-}i\text{-}Pr)_2(CH_2SiMe_3)_4$.[6] With use of the molybdenum(IV) alkoxide $Mo_2(O\text{-}i\text{-}Pr)_8$ (Mo=Mo),[7] a similar procedure gave an intense blue solution at −78 °C in pentane. When the mixture was allowed to warm up to room temperature, the color faded to yellow-brown. Analysis of the product showed only two molybdenum alkyl compounds, **1** and $Mo(CH_2SiMe_3)_3(\equiv CSiMe_3)$ (**2**)[3] in approximately equimolar amounts. None of the purple $Mo(CH_2SiMe_3)_3(=CHSiMe_3)$ obtained on alkylation of $MoCl_5$[3] appeared to be present in the final mixture. This apparently clean disproportionation (eq 1) contrasts with the simple substitution chemistry found for chromium(IV) alkoxides.[1a]

$$3Mo_2(O\text{-}i\text{-}Pr)_8 + 24LiCH_2SiMe_3 \rightarrow 2\,\mathbf{1} + 2\,\mathbf{2} + 24LiO\text{-}i\text{-}Pr + 4SiMe_4 \quad (1)$$

In contrast to molybdenum and chromium, alkylation of alkoxides of niobium and tantalum rarely leads to total substitution. Table I lists the results of the reaction of various alkoxides and lithium alkyls under different conditions. A similar procedure was carried out for the isolation of all of the products and a typical synthesis is outlined.[8] Alkylation with methyllithium in hydrocarbon solvents is complicated both by the low solubility of this reagent and also the instability of some of the products. Addition of $LiCH_3$ (3 equiv) to $Ta(O\text{-}i\text{-}Pr)_5$ in benzene gave a clear yellow solution after 1 h. Removal of solvent followed by distillation (70 °C (10^{-3} mm)) gave **5** as a colorless liquid. Solutions of **5** in benzene were stable over several weeks as monitored by ^1H NMR, but in the presence of excess $LiCH_3$ decomposition with the evolution of CH_4 occurred over a few hours. We believe this to be due to the slow formation of $TaMe_5$ or $Ta(O\text{-}i\text{-}Pr)Me_4$, the former is known to be unstable at room temperature.[9] A similar reactivity pattern was observed for all of the tantalum and niobium alkoxides with $LiCH_3$.

When the two reagents $LiCH_2SiMe_3$ and $LiCH_2CMe_3$ were used, much more stable products were obtained. From Table I it can be seen that typically the trisubstituted product is given. However, in one case, the reaction of $Ta(OMe)_5$ with $LiCH_2SiMe_3$ the tetrasubstituted product **3** could be isolated. When monitored by ^1H NMR spectroscopy, solutions of the reagents showed no indication of intermediates.

The ^1H NMR spectra of the trisubstituted compounds are temperature independent, showing only one type of alkyl and alkoxide (aryl oxide) ligand down to −90 °C (90 MHz). In the case of the trineopentyl and tris(trimethylsilyl) complexes the methylene groups remain as a singlet over this temperature range. The spectra are thus consistent with structure I, in which the two oxygen donor ligands are trans to each other and occupy axial positions in a trigonal-bipyramidal coordination geometry about the metal atom. This geometry is that proposed for $MCl_2(R)_3$ compounds of Ta and Nb.[10]



I

With the extremely bulky 2,6-di-*tert*-butylphenoxide ligand, the trimethyl compound **9** can be synthesized from $Ta(OC_6H_3\text{-}t\text{-}Bu_2)_2Cl_3$ (**11**).[12] A preliminary structure de-

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(3) Andersen, R. A.; Chisholm, M. H.; Gibson, J. F.; Reichert, W. W.; Rothwell, I. P.; Wilkinson, G. *Inorg. Chem.* **1981**, *20*, 3934.

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(5) To a solution of $Mo_2(O\text{-}i\text{-}Pr)_6$ (1.50 g, 2.8 mmol) in pentane (20 mL) was added $LiCH_2SiMe_3$ (1.6 g, 17.0 mmol) in pentane (5 mL) at 0 °C. The mixture was stirred for 0.5 h and filtered. Removal of solvent under vacuum gave an orange product (1.92 g) contaminated with small amounts of LiO-*i*-Pr. Sublimation of this mixture allowed isolation of pure $Mo_2(CH_2SiMe_3)_6$ (1.51 g, 74%) as orange crystals. Problems with LiO-*i*-Pr contaminants could be eliminated by using $Mg(CH_2SiMe_3)_2$, although the reaction was much slower.

(6) Chisholm, M. H.; Rothwell, I. P. *J. Am. Chem. Soc.* **1980**, *102*, 5950.

(7) Chisholm, M. H.; Reichert, W. W.; Thornton, P. *J. Am. Chem. Soc.* **1978**, *100*, 2744.

(8) **$Ta(O\text{-}i\text{-}Pr)_2(CH_2SiMe_3)_3$.** A mixture of $Ta(O\text{-}i\text{-}Pr)_5$ (2.1 g, 5.3 mmol) and $LiCH_2SiMe_3$ (6.4 g, 6.8 mmol) in benzene (50 mL) was stirred for 1 h. Removal of solvent followed by sublimation, 80 °C (10^{-3} torr), gave the product as a white solid (1.93 g, 66%). Anal. Calcd for $TaSi_3O_2C_{18}H_{47}$: C, 38.55; H, 8.44. Found: C, 38.72; H, 8.95.

(9) Schrock, R. R. *J. Organomet. Chem.* 1976, *122*, 209.

(10) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.

(11) **$Ta(OC_6H_3Me_2)_5$.** This compound is prepared in excellent yield by the reaction of $LiOC_6H_3Me_2$ (prepared as a white solid from $HOC_6H_3Me_2$ and Li-*n*-Bu in hexane) with $TaCl_5$ (6/1 ratio) in benzene over 2 h. Evaporation, followed by extraction with pentane gave the pure product as a white solid. Anal. Calcd for $TaO_5C_{40}H_{45}$: C, 61.07; H, 5.77. Found: C, 60.92; H, 5.57.

termination on **9** shows structure I implied by NMR data.[17] Addition of $LiCH_2SiMe_3$ to **11** leads to the generation of Me_4Si and the formation of the alkylidene compound **10**.[14] This behavior is similar to that observed for the compound $Ta[N(SiMe_3)_2]_2Cl_3$.[15] The facile α-hydrogen abstraction to generate **10** contrasts to the stability of **8a**, which contains 2,6-dimethylphenoxide and does not generate Me_4Si when heated at 120 °C for days in sealed ^1H NMR tubes. This is a clear indication that the α-hydrogen abstraction is sterically induced as proposed by Schrock and coworkers.[10]

Registry No. **1**, 34439-17-3; **2**, 78638-61-6; **3**, 82182-15-8; **4**, 82182-16-9; **5**, 82182-17-0; **6a**, 82182-18-1; **6b**, 82182-19-2; **7**, 82182-20-5; **8a**, 82182-21-6; **8b**, 82182-22-7; **9**, 82182-23-8; **10**, 82182-24-9; **11**, 82190-58-7; $Ta(OC_6H_3Me_2)_5$, 82182-25-0; $TaCl_5$, 7721-01-9; $Ta(OMe)_5$, 865-35-0; $Nb(O\text{-}i\text{-}Pr)_5$, 18368-80-4; $Nb(OC_6H_3Me_2)_5$, 82182-26-1; $Ta(O\text{-}i\text{-}Pr)_5$, 16761-83-4; $Me_2(O\text{-}i\text{-}Pr)_6$, 62521-20-4; $Mo_2(O\text{-}i\text{-}Pr)_8$, 66526-46-3; 1,2-$Mo_2(O\text{-}i\text{-}Pr)_2(CH_2SiMe_3)_4$, 75059-92-6; $LiCH_2SiMe_3$, 1822-00-0; $Mg(CH_2SiMe_3)_2$, 51329-17-0; $LiOC_6H_3Me_2$, 24560-29-0; $LiOC_6H_3\text{-}t\text{-}Bu_2$, 55894-67-2; $LiCH_3$, 917-54-4.

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[12] Addition of an excess of $LiOC_6H_3\text{-}t\text{-}Bu_2$ to $TaCl_5$ in benzene gives $Ta(OC_6H_3\text{-}t\text{-}Bu_2)_2Cl_3$ (**11**) as an orange solid after 1 h. No further substitution takes place. Filtration, removal of solvent, and washing with pentane gave the pure product. Anal. Calcd for $TaCl_3O_2C_{28}H_{42}$: C, 48.19; H, 6.07; Cl, 15.24. Found: C, 48.82; H, 6.13; Cl, 14.98%.

[13] Addition of an excess of $LiCH_3$ to (**11**) gave $Ta(OC_6H_3\text{-}t\text{-}Bu_2)_2(CH_3)_3$ (**9**) over 1 h. Removal of solvent and extraction with pentane gave the product as a white crystalline solid. Continued exposure to $LiCH_3$ for longer periods of time resulted in a black suspension from which **9** could be isolated although in much reduced yield.

[14] Addition of 3 equiv of $LiCH_2SiMe_3$ to **11** at −60 °C in hexane gave a yellow suspension. When slowly warmed to 25 °C, the solution darkened to a light brown color. Filtration and reduction of the volume followed by cooling to −15 °C gave the product **10** as yellow crystals. In the ^{13}C NMR spectrum, the alkylidene carbon resonated at δ 237.1 while in the ^1H NMR spectrum the $Ta{=}CHSiMe_3$ proton was observed as a singlet at δ 8.60.

[15] Andersen, R. A. *Inorg. Chem.* **1979**, *97*, 2935.

[16] ^1H NMR data recorded in benzene-d_6 at 35 °C: **3**, $\delta(OCH_3)$ 3.83 (s), $\delta(TaCH_2)$ 0.94 (s), $\delta(SiMe_3)$ 0.23 (s); **4**, $\delta(OCH_3)$ 4.21 (s), $\delta(TaCH_2)$ 0.95 (s), $\delta(CMe_3)$ 1.17 (s); **5**, $\delta(OCHMe_2)$ 4.64 (septet), $\delta(OCHMe_2)$ 1.27 (d), $\delta(TaCH_3)$ 0.76 (s); **6a**, $\delta(OCHMe_2)$ 4.82 (septet), $\delta(OCHMe_2)$ 1.39 (d), $\delta(TaCH_2)$ 0.66 (s), $\delta(SiMe_3)$ 0.18 (s); **6b**, $\delta(OCHMe_2)$ 4.79 (septet), $\delta(OCHMe_2)$ 1.42 (d), $\delta(NbCH_2)$ 1.17 (s), $\delta(SiMe_3)$ 0.18 (s); **7**, $\delta(C_6H_3)$ 6.53–7.1 (m), $\delta(C_6H_3Me_2)$ 2.51 (s), $\delta(TaCH_2)$ 1.72 (s), $\delta(CMe_3)$ 1.10 (s); **8a**, $\delta(C_6H_3)$ 6.81–7.15 (m), $\delta(C_6H_3Me_2)$ 2.50 (s), $\delta(TaCH_2)$ 1.11 (s), $\delta(SiMe_3)$ 0.07 (s); **8b**, $\delta(C_6H_3)$ 6.78–7.20 (m), $\delta(C_6H_3Me_2)$ 2.48 (s), $\delta(NbCH_2)$ 1.73 (s), $\delta(SiMe_3)$ 0.08 (s); **9**, $\delta(C_6H_3)$ 6.7–7.2 (m), $\delta(C_6H_3\text{-}t\text{-}Bu_2)$ 1.45 (s), $\delta(TaCH_3)$ 1.19 (s); **10**, $\delta(C_6H_3)$ 6.6–7.1 (m), $\delta(C_6H_3\text{-}t\text{-}Bu_2)$ 1.41 (s), $\delta(Ta{=}CH)$ 8.60 (s), $\delta(TaCH_2)$ 1.35 (s), $\delta(SiMe_3)$ 0.21 (s) and 0.39 (s).

[17] Huffman, J. C., Molecular Structure Center, Indiana University, private communication.

Transformation of η^3-Allyl to μ-η^1,η^3-Allylidene in Certain Ruthenium Complexes

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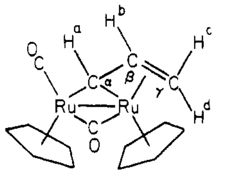
Summary: The passing of an acetone-hexane solution of $Ru(CO)(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)$ through a deactivated silica gel column gives $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHCHCH_2)(\eta^5\text{-}C_5H_5)_2]$ by a process involving η^3-allyl to μ-η^1,η^3-allylidene transformation.

Recently, Knox et al.[1] described the preparation of the methylcarbyne complex $[Ru_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CMe)(\eta^5\text{-}C_5H_5)_2]^+BF_4^-$ and its photolytic (UV) reaction with ethylene or propene to give $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}C(Me)C(R)CH_2)(\eta^5\text{-}C_5H_5)_2]$ (**1**, R = H, Me).[2] In this reaction, a substituted μ-η^1,η^3-allylidene ligand is formed by the interaction of olefins with μ-methylcarbyne at a diruthenium center. The current communication describes a facile route to the parent μ-η^1,η^3-allylidene complex by the interconversion of certain (η^3-allyl)ruthenium complexes. This procedure constitutes an unprecedented one-step synthetic route to a μ-carbene, a ligand thought to play an important role during the Fischer–Tropsch synthesis.

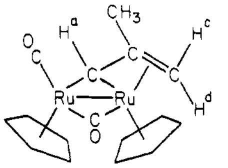
A solution of $Ru(CO)(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)$ (**2**; mixture of isomers) in acetone–hexane (1:9, v/v) when passed through a deactivated silica gel column gives the yellow parent μ-η^1,η^3-allylidene complex $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHCHCH_2)(\eta^5\text{-}C_5H_5)_2]$ (**3**) in 65% yield. The methyl derivative $[Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHC(Me)CH_2)(\eta^5\text{-}C_5H_5)_2]$ (**4**) was prepared from $Ru(CO)(\eta^3\text{-}CH_2C(Me)CH_2)(\eta^5\text{-}C_5H_5)$ by the same procedure in 64% yield.

The properties of **3** and **4** are as follows: Complex **3**: pale yellow; mp 196–198 °C; IR ($CHCl_3$) ν(CO) 1946 (vs), 1769 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.35 (ddd, J = 0.8, 1.2, 6.2 Hz, 1 H), 5.24 (s, 5 H), 4.93 (s, 5 H), 4.72 (ddd, J = 6.2, 6.9, 9.0 Hz, 1 H), 2.65 (ddd, J = 1.2, 2.8, 6.9 Hz, 1 H), −0.02 (ddd, J = 0.8, 2.8, 9.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) spectrum (gate-decoupled and proton-coupled spectral data for the μ-η^1,η^3-allylidene and cyclopentadienyl carbon nuclei) δ 152.82 (d, J = 98.5 Hz), 88.32 (d, J = 60.3 Hz), 83.38 (d, J = 64.7 Hz), 79.12 (J = 51.5 Hz), 39.58 (dd, J = 6.6, 30.1 Hz). Anal. Calcd for $C_{15}H_{14}O_2Ru_2$: C, 41.93; H, 3.39. Found: C, 42.08; H, 3.27. Complex **4**: pale yellow; mp 197–199 °C; IR ($CHCl_3$) ν(CO), 1945 (vs), 1770 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.20 (dd, J = 0.75, 1.6 Hz, 1 H), 5.27 (s, 5 H), 4.91 (s, 5 H), 2.73 (dd, J = 1.6, 2.5 Hz, 1 H), 1.97 (s, 3 H), −0.05 (dd, J = 0.75, 2.5 Hz, 1 H). Anal. Calcd for $C_{16}H_{16}O_2Ru_2$: C, 43.25; H, 3.61. Found: C, 43.31; H, 3.65.

The spectroscopic (^1H NMR and IR) properties of the new complexes (**3** and **4**) are rather similar to those observed for **2** (R = H, Me),[2] where an X-ray crystal structure (**2**, R = Me) was reported. It was claimed that neither of the three bonding representations of the μ-η^1,η^3-allylidene ligand (**5**–**7**) conflict with the crystallographic date of **2** (R = Me). On the other hand, distinction between these representations was made possible by the combination of ^1H and ^{13}C NMR spectroscopic studies on the parent ligand in **3** and the monosubstituted ligand in **4**.



3



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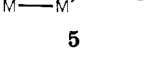

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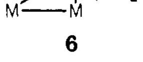

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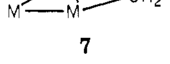

7

Rigorous assignments of the ^1H NMR chemical shifts of the μ-η^1,η^3-allylidene ligands in **3** and **4** were accomplished by spin decoupling experiments at both 80 and 270 MHz. In the spectrum of **3**, the respective proton H^a (δ

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[1] Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Naish, P. J.; Orpen, A. G.; Plaas, D.; Taylor, G. E. *J. Organomet. Chem.* **1980**, *198*, C43.

[2] Dyke, A. F.; Guerchais, J. E.; Knox, S. A. R.; Roue, J.; Short, R. L.; Taylor, G. E.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 537.

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