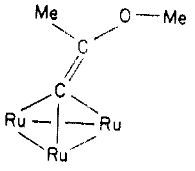
(s), 1952 (vs), and 1899 (m) cm^{-1}) and one characteristic of bridging CO (1750 (m) cm^{-1}). The spectrum of a solid sample in a Nujol mull is similar. The ^{13}C NMR spectrum of 1 in CD_2Cl_2 at −90 °C contains three sharp carbonyl resonances of equal intensity at 273.3, 204.0, and 202.3 ppm and two higher field resonances for the β- and α-carbons of the CCO at 159.1 and −28.3 ppm. The overall intensity pattern is 3:3:3:1:1. The ^{13}C NMR spectrum of a sample enriched to ca. 30% in ^{13}C at all carbons clearly shows the peaks at 159.1 and −28.3 ppm to have superimposed doublets (J_{CC} = 96 Hz). The spectral data are consistent with the structure of the compound in the solid state.

Protonation of 1 with one equivalent of fluorosulfonic acid at −35 °C yields compound 2 which displays a singlet at −17.51 ppm in the ^1H NMR, indicating that the first proton attaches to the metal framework instead of the α-carbon of CCO, as in the case of $[Fe_3(CO)_9CCO]^{2-}$ (Scheme II).[2] The infrared spectrum of 2 in diethyl ether shows that it contains no bridging carbonyls (ν_{CO} = 2069 (w), 2032 (s), 2017 (m), 1999 (vs), 1969 (m), and 1927 (w) cm^{-1}). Addition of a second equivalent of acid gives the previously characterized[6] $H_2Ru_3(CO)_9CCO$, identified by its infrared, mass, and ^1H NMR spectra.[11] Therefore, protonation of 1 occurs exclusively on the metal framework. Reaction of 1 with the carbocation reagent $CH_3OSO_2CF_3$ leads to attack of the oxygen and the β-carbon of the CCO to give $Ru_3(CO)_{10}C{=}C(OMe)Me$, 3, based on spectroscopic evidence[12] as well as a crystal structure determination.



3

The cationic ketenylidenes $[H_3Os_3(CO)_9CCO]^+$, $[H_3Ru_3(CO)_9CCO]^+$, and $[Co_3(CO)_9CCO]^+$ are susceptible to nucleophillic attack by methanol at the β-carbon of the CCO ligand.[1,5,7] In contrast, 1 is stable in methanol and no reaction is observed with excess methoxide ion.

As seen for $[Fe_3(CO)_9CCO]^{2-}$, the ruthenium ketenylidene also undergoes facile cluster building reactions. Hence reaction of 1 with $Fe_2(CO)_9$ yields a dianion, presumably $[Ru_3FeC(CO)_{12}]^{2-}$, which displays a characteristic carbide resonance in the ^{13}C NMR at 440.45 ppm downfield from Me_4Si. Protonation of this compound gives $H_2FeRu_3C(CO)_{12}$, identified by mass spectrum.[13]

In summary, the overall character of the anionic ketenylidene $[Ru_3(CO)_9CCO]^{2-}$, 1, is that of a nucleophile. The CCO moiety of 1 is susceptible to attack by the carbocation reagent $CH_3SO_3CF_3$, although the site of attack is different than in $[Fe_3(CO)_9CCO]^{2-}$. Owing to the greater basicity of ruthenium over iron, 1 is protonated on the metal rather than the α-carbon as is observed for $[Fe_3(CO)_9(CCO)]^{2-}$. Unlike the previously reported neutral ruthenium and osmium ketenylidenes, 1 appears to have negligible electrophilic character at the β-C of the CCO. Additionally, compound 1 undergoes facile cluster building reactions, which should provide a convenient route to the synthesis of a wide range of mixed-metal carbide cluster compounds.

Acknowledgment. The research was supported by the NSF. The mass spectroscopy analysis program MASPAN was kindly provided by M. Andrews and H. D. Kaesz, UCLA. M.J.S. was the recipient of an ARCO fellowship. M.J.S. thanks Joseph A. Hriljac for helpful discussions.

Registry No. 1, 97150-45-3; **2**, 97150-46-4; **3**, 97150-47-5; $H_2Ru_3(CO)_9CCO$, 90990-76-4; $[Ru_3FeC(CO)_{12}][PPN]_2$, 97150-49-7; $Fe_2(CO)_9$, 15321-51-4; $[Ru_3(CO)_{10}(\mu^3\text{-}COCOCH_3)]PPN$, 97150-51-1; $[Ru_3(CO)_{10}(\mu\text{-}Co)][PPN]_2$, 97150-52-2; $[OS_3(CO)_9(CCO)]^{2-}$, 97150-53-3; CH_3COCl, 75-36-5.

Supplementary Material Available: Complete listings of positional and thermal parameters, bond angles, bond distances, and observed and calculated structure factors for $[Ru_3(CO)_9(CCO)][PPN]_2$ (112 pages). Ordering information is given on any current masthead page.

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[11] For $H_2Ru_3(CO)_9CCO$: ν_{CO} (pentane) 2120 (w), 2086 (m), 2061 (s), 2040 (mw), 2016 (m)cm^{-1}. A MASPAN analysis of the parent envelope centered at 599 mass units in the 15-EV electron-impact mass spectrum yields an agreement factor of R = 5.2% for $H_2Ru_3(CO)_{10}C$; ^1H NMR (CD_2Cl_2) −17.99 ppm relative to Me_4Si.

[12] For $Ru_3(CO)_{10}CC(OMe)Me$: ν_{CO} (pentane): 2093 (w), 2061 (vs), 2041 (s), 2024 (s), 2004 (m) (sh), 1918 (w) cm^{-1}; ^1H NMR (CD_2Cl_2) 3.81, 2.36 ppm relative to Me_4Si; ^{13}C NMR (CD_2Cl_2, −90 °C) 263.0 (br), 195.6, 192.8 ($^1J_{CC}$ = 55 Hz), 168.7 ($^1J_{CC}$ = 55 Hz) ppm relative to Me_4Si; 70-eV EI mass spectrum, 655 mass units, successive loss of 10 CO's.

[13] For $H_2Ru_3FeC(CO)_{12}$: 70-eV EI mass spectrum shows parent ion envelope centered at 709 mass units and successive loss of 12 CO's.

Synthesis of 1-Phenylarsole and 1-Phenylstibole

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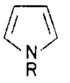
Summary: Hydrogenation of 1,4-diiodobuta-1,3-diyne with diimide gave 1(*Z*),4(*Z*)-diiodobuta-1,3-diene which on treatment with *n*-butyllithium followed by phenylarsenic dichloride or phenylantimony dichloride afforded 1-phenylarsole or 1-phenylstibole, respectively.

The pyrrole analogues 2–5 are of general interest for testing concepts of aromaticity.[1] While 1-phenylphosphole is available,[2,3] only more highly substituted derivatives of 3–5[4-7] have been reported. Since the properties of the parent ring systems may be masked by substitution, a preparation of the C-unsubstituted heteroles 3–5 would be a valuable addition to the study of element–carbon conjugation. We now wish to report on a general synthesis which allows preparation of the 1-phenylheteroles of the group 5 elements.



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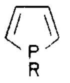

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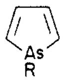

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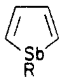

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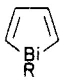

5

Since perphenylheteroles 7 have been prepared from the reaction of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (6)

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[1] For a critical discussion of phosphole aromaticity see: Quinn, L. D. "The Heterocyclic Chemistry of Phosphorus: Systems Based on the Phosphorus-Carbon Bond"; Wiley: New York, 1981; pp 406–414.

[2] Märkl, G.; Potthast, R. *Tetrahedron Lett.* **1968**, 1755.

[3] Mathey, F.; Mankowski-Favelier, R. *Org. Magn. Reson.* **1972**, *4*, 171.

[4] Leavitt, F. C.; Manuel, T. A.; Johnson, F.; Matternas, L. U.; Lehman, D. S. *J. Am. Chem. Soc.* **1960**, *82*, 5099. Braye, E. H.; Hübel, W.; Caplier, I. *J. Am. Chem. Soc.* **1961**, *83*, 4406.

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[7] Ashe, A. J., III; Drone, F. J. *Organometallics* **1984**, *3*, 495.

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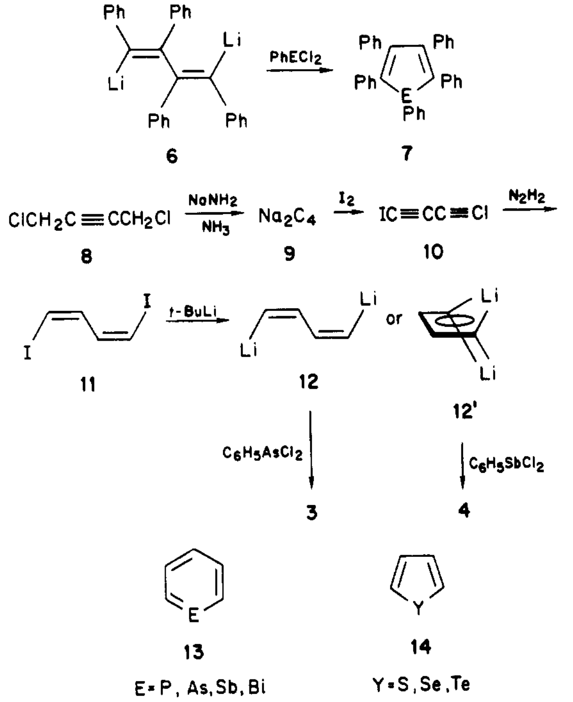
with phenylelement dihalides,[4] we decided to explore a route using 1,4-dilithiobutadiene. 1,4-Dichloro-2-butyne (**8**) may be dehydrohalogenated with excess sodamide in liquid ammonia to give the disodium salt of diacetylene **9**,[8] which on treatment with iodine affords 55% of 1,4-diiodobutadiyne (**10**).[9] Although **10** is *sensitive to shock and heat*,[9] we have prepared up to 25-g batches without incident.[10] Diimide hydrogenation of **10** in pentane is achieved by the portionwise addition of excess potassium azobiscarboxylate in methanol/pyridine followed by acetic acid over 24 h.[11] The course of the reaction is conveniently followed by ^{1}H NMR spectroscopy. Pure 1(*Z*),4(*Z*)-diiodobuta-1,3-diene (**11**) was obtained in 55% yield by recrystallization from pentane: mp 33–35 °C; ^{1}H NMR (CD_2Cl_2) δ 6.73 (m, 2 H), 6.99 (m, 2 H);[12] mass spectrum, *m/e* 306 (M^+), 179 ($M^+ - I$); IR (neat, cm^{-1}) 3090, 1540, 660. Lithiation of diiodide **11** with *n*-butyllithium in diethyl ether at 0 °C gave a low conversion to the desired dilithium compound **12**. Whether **12** has the bridged structure **12′** predicted on theoretical grounds remains to be determined.[12]



The reaction of 1,4-dilithiobutadiene (prepared from 9 mmol of **11**) with an equivalent of phenylarsenic dichloride in diethyl ether gave a 15% yield (based on **11**) of 1-phenylarsole (**3**), which was isolated as a light yellow oil by Kugelrohr distillation at 95 °C (0.005 torr). The arsenic heterocycle is sensitive to oxygen but can be stored at 25 °C under an inert atmosphere. The arsole shows the following mass spectral and UV data: mass spectrum (CI-CH_4), *m/e* 205 (M + 1); UV (pentane) λ_{max} 274 (ϵ 4700), 223 nm (ϵ 6400). Similar reaction of **12** with phenylantimony dichloride in diethyl ether gave 10% (based on **11**) of 1-phenylstibole (**4**) which was isolated as a yellow oil by Kugelrohr distillation at 70 °C (0.005 torr). The rather labile stibole darkens and slowly resinifies on standing at 25 °C under an inert atmosphere. The stibole shows the following mass spectral and UV data: mass spectrum (CI-CH_4), *m/e* 253 (M + 1 for $C_{10}H_9{}^{123}Sb$); UV pentane λ_{max} 283 (ϵ 2800), 230 (ϵ 10 000), 216 nm (ϵ, 16 700).

Table I. ^{1}H NMR Chemical Shift Values for the 1-Phenylheteroles $C_4H_4EC_6H_5$

E	$\delta(H_2,H_5)$	$\delta(H_3,H_4)$	$\delta(C_6H_5)$
N (1)[a]	6.94	6.19	7.3
P (2)[b]	7.0	6.47	7.0
As (3)[c]	7.20[d,e]	7.25[d,e]	7.29–7.35
Sb (4)[c]	7.53[d,i]	7.57[d,f]	7.25–7.50

[a] Aldrich NMR Catalog, 2, 449D. [b] Reference 2. [c] Measured in CD_2Cl_2 solvent relative to internal Me_4Si at 360 MHz. [d] The relative assignment of $\delta(H_2,H_3)$ is uncertain. [e] Satisfactory spectral simulation using the Bruker PANIC program is achieved by using J_{23} = 7.5 Hz, J_{24} = 1.0 Hz, J_{25} = 3.0 Hz, and J_{34} = 2.0 Hz. [f] Satisfactory spectral simulation for J_{23} = 8.5 Hz, J_{24} = 1.0 Hz, J_{25} = 3.0 Hz, and J_{34} = 2.0 Hz.

Table II. ^{13}C NMR Chemical Shift Values for the 1-Phenylheteroles $C_4H_4EC_6H_5$

E	$\delta(C_2)$	$\delta(C_3)$	$\delta(C_i)$	$\delta(C_o)$	$\delta(C_m)$	$\delta(C_p)$
N (1)[a]	119.0	110.1	140.4	120.2	129.1	125.3
P (2)[b]	135.1	136.7	129.6	133.3	128.3	128.9
As (3)	140.0[c]	142.2[c]	134.8	133.5	129.0	129.0
Sb (4)	142.0[c,d]	147.1[c,d]	134.6	136.3	129.1	129.0

[a] Begtrup, M. *Acta Chem. Scand.* **1973**, *27*, 3101. [b] Reference 15. [c] Relative assignment uncertain. [d] Assignment made by comparison with the spectrum of the 2,5-dimethyl-1-phenylstibole.[6]

The synthesis of the unsubstituted heteroles **3** and **4** makes small quantities of these materials available for comparison with **1** and **2**. Thus the proton and carbon NMR chemical shift values of **1**, **2**, **3**, and **4** are compared in Tables I and II. The proton NMR spectra of the heteroles show a progressive downfield shift of the ring protons with increasing atomic number of the heteroatom. Indeed the signals for the ring protons of **4** are shifted downfield from those of the phenyl protons. It does not seem likely that this effect can be ascribed solely to ring current. The effect seems similar to that observed for the group 5 six-membered heterocycles **13**[14] and the group 6 five-membered ring heterocycles **14**.[15] In the case of the heterobenzene **13**, the downfield shift was shown to arise from the anisotropy of the group 5 heteroatom.[14]

The ^{13}C NMR spectra of **2**,[16] **3**, and **4** summarized in Table II are very similar.[17] The small range of values for the ring carbon shifts in olefinic region contrasts with the large progressive shifts to low field which were observed for the α-carbon signals of the heterobenzenes. Phosphaalkenes[18] and arsaalkenes[19] also show very low field signals. Thus this difference between the five- and six-membered ring group 5 heterocycles may come from differences in the degree of element–carbon multiple bonding between the two sets of compounds. Certainly a detailed

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(9) Heilbronner, E.; Hornung, V.; Maier, J. P.; Kloster-Jensen, E. *J. Am. Chem. Soc.* **1974**, *96*, 4252.

(10) For larger scale preparations **10** is not isolated. Pentane is added to the liquid ammonia reaction mixture. After evaporation of the ammonia, this pentane solution of **10** is hydrogenated to **11**.

(11) For a similar procedure see: Lüthy, C.; Konstantin, P.; Untch, K. G. *J. Am. Chem. Soc.* **1978**, *100*, 6211.

(12) The H NMR consists of an AA′BB′ pattern.

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theoretical investigation of the relationship between carbon NMR shifts and element–carbon multiple bonding would be helpful.

Acknowledgment. Support of our work by the A.F. O.S.R. (Grant No. 81-099) is gratefully acknowledged.

Registry No. **3**, 97102-15-3; **4**, 97102-16-4; **8**, 821-10-3; **10**, 7572-29-4; **11**, 97102-17-5; $C_6H_5AsCl_2$, 696-28-6; $C_6H_5SbCl_2$, 5035-52-9.

Reactions of Chiral (α-Methoxyvinyl)rhenium Complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3){=}CHR)$ with Alkyl Halides. Efficient 1,3-Asymmetric Induction

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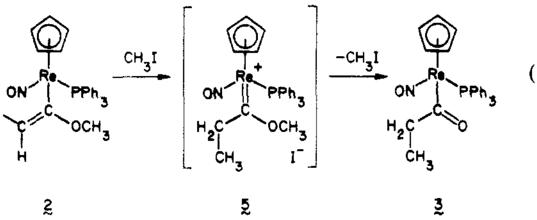
Received April 2, 1985

Summary: α-Methoxyvinyl complexes (*Z*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3){=}CHR)$ are readily alkylated ($C_6H_5CH_2Br$, CH_3I) to give acyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCHRR')$ with high diastereoselectivity; the stereochemistry of these reactions, and probable transition-state geometries, are established by an X-ray crystal structure of the product (*SR*,*RS*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH(CH_3)CH_2C_6H_5)$.

We recently described the synthesis of chiral vinylrhenium complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}CHR)$.[1] These reacted with strong electrophiles (E^+X^-) such as CH_3SO_3F to give alkylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHCHRE)]^+X^-$ containing a new asymmetric carbon. Although excellent 1,3-asymmetric induction was achieved, the synthetic utility of this chemistry was limited by the modest nucleophilicity of the vinyl complexes. At that time, we proposed that an α-oxygen substituent might provide enhanced reactivity and consequently broader applicability of this chemistry in asymmetric synthesis. In this communication, we report the successful realization of these goals with α-methoxyvinyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3){=}CHR)$. Similar observations have also been communicated by Davies with related iron complexes.[2]

Treatment of methoxycarbene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}C(OCH_3)CH_3)]^+PF_6^-$ (**1**) with NaH (THF, 25 °C) gave, after workup, α-methoxyvinyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3){=}CH_2)$ (**2**)[4] in 75% yield. Reaction of **2** with CH_3I (CH_2Cl_2, 12 h) occurred readily at room temperature to give propionyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2CH_3)$ (**3**, eq 1)[3] and lesser quantities of acetyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_3)$[3] and the dimethylation product, isobutyroyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH(CH_3)_2)$ (**4**)[4] (spectroscopic ratio after 36 h: 42:33:25).

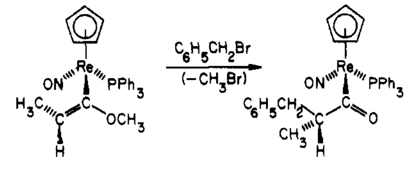


(1)

2 **5** **3**

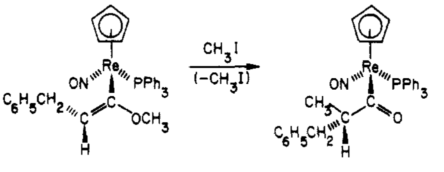
The conversion **2** → **3** is proposed to proceed via the methoxycarbene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}C(OCH_3)CH_2CH_3)]^+I^-$ (**5**, eq 1). Indeed, when this reaction is monitored by ^1H NMR in CD_2Cl_2, an intermediate with plausible resonances for **5** is observed (δ (−35 °C, two isomers)[3] 5.71, 6.01 (s, C_5H_5), 3.70, 4.15 (s, OCH_3), 0.79, 1.11 (t, CCH_3)). Subsequently, iodide ion effects O-demethylation, analogously to previous observations with cationic iron methoxycarbene complexes.[5] The acyl byproducts which accompany **3** likely arise via proton transfer from **5** to **2**. Indeed, the deprotonation product of **5**, **6** (see below), is also observed by ^1H NMR during the course of eq 1. Malisch has reported similar side reactions in alkylations of iron α-methoxyvinyl complexes.[6]

Having established the ready nucleophilicity of α-methoxyvinyl complexes, we next examined their effectiveness in 1,3-asymmetric induction reactions. The substrates (*Z*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3){=}CHCH_3)$ (**6**, eq 2)[4] and (*Z*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3){=}CHCH_2C_6H_5)$ (**7**, eq 3)[4] were isolated in 72% and 81% overall yields by reactions of the corresponding acyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2R)$ with first $(CH_3)_3O^+PF_6^-$ (CH_2Cl_2, 25 °C) to give methoxycarbene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}C(OCH_3)CH_2R)]^+PF_6^-$ and then the base DBU.[7] By all spectroscopic criteria, **6** and **7** were isomerically pure. Both exhibited a 33 ± 5% ^1H NOE enhancement[8] of the vinyl hydrogen resonance upon irradiation of the α-methoxy resonance, as would be expected of *Z* geometric isomers.[2a] The structure of **7** was verified by X-ray crystallography.[9]



(2)

6 (*SR*,*RS*)-**8**



(3)

7 (*SS*,*RR*)-**8**

Complex **6** was treated with $C_6H_5CH_2Br$ (CH_2Cl_2; 25 °C, 12 h, and then 50 °C, 2 h). Acyl complex (*SR*,*RS*)-(η^5-

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(4) Microanalytical, IR, and NMR (^1H, ^{13}C, ^{31}P) data for each new compound are given in the supplementary material. In compounds with two chiral centers, the absolute configuration at rhenium is specified first.

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(7) When the reactions of **6**, **7**, and related complexes with DBU and other bases were monitored by ^{31}P NMR at −78 °C, transients believed to be *E* geometric isomers were observed (*E*/*Z* as high as 88:12). These isomerized (in a process that was inhibited by added NaH) to *Z* isomers upon warming. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

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(9) The X-ray crystal structure of **7** will be described in a separate publication.