of **29** were obtained (35 mg, 79.9%, mp 143 °C).

Compound **23** (30 mg, 0.041 mmol) was dissolved in THF (0.75 mL) in an 8-mm NMR tube. A solution of sodium trifluoroethoxide was prepared by the addition of sodium (1.6 g, 0.070 mmol) to a solution of trifluoroethanol (9.0 mL, 0.116 mmol) in THF (100 mL). A 1.0-mL portion of this solution was added to the NMR tube and P–P bond cleavage was followed by ^{31}P NMR spectroscopy. A precipitate of NaCl was observed. Carbon tetrachloride (200 μL, 207 mmol) was added, and the complete conversion to **30** was monitored by ^{31}P NMR spectroscopy. Product **30** was isolated by column chromatography with elution by dichloromethane–hexane (1:3). An orange oil (10 mg, 22.8%) was obtained.

For **29**: IR 2980 (w, CH), 1250 (vs, br, PN), 600 (s, PCl) cm^{-1}; ^1H NMR δ 4.843, 4.803 (both m, 4 H); ^{31}P NMR 35.0 (t), 21.1 (d, J_{PNP} = 17.4 Hz) ppm; MS, *m/e* calcd for $C_{10}H_8N_6Cl_{10}FeP_6$ 803.5471, found 803.5496 (3.2 ppm).

For **30**: IR 2980 (w, CH), 1250 (vs, br, PN) cm^{-1}; ^1H NMR δ 4.620, 4.597 (both m, 4 H), 4.296 (dm, 8 H); ^{31}P NMR; 35.6 (t), 16.4 (d, J_{PNP} = 56.2 Hz), ppm; ^{19}F NMR 37 (m) ppm; MS, *m/e* calcd for $C_{30}H_{28}N_6Fe_{30}FeO_{10}P_6$ 1444, found 1444.

X-ray Structure Determination. Our general X-ray structure technique has been described in earlier papers,[1a,11] and only the details related to the present work will be given here. A crystal of **6a**, with dimensions 0.31 × 0.25 × 0.30 mm, obtained from a saturated solution in hexane, was mounted along the longest axis. A summary of the important crystallographic data is presented in Table I. The drift correction shown in the table was used to allow for slight crystal motion or temperature changes during data collection. A crystal of **10b**, with dimensions 0.29 × 0.31 × 0.62 mm, was obtained from a solution in dichloromethane–hexane and was cut for analysis and mounted along the longest axis. Crystals of **12b** were obtained by temperature-gradient vacuum sublimation at 25–50 °C (10^{-3} torr). A single, well-formed crystal of dimensions 0.30 × 0.32 × 0.60 mm was chosen and mounted along the longest axis. A crystal of **23**, with dimensions 0.15 × 0.27 × 0.40 mm, was obtained from dichloromethane–hexane solution and was mounted along the longest axis.

The structures were solved by Patterson heavy-metal techniques. Subsequent cycles of least-squares refinement and difference Fourier syntheses yielded the remaining non-hydrogen atoms. In the final cycles of full-matrix least-squares refinement, all non-hydrogen atom positional parameters and anisotropic thermal parameters were refined. The positional and thermal parameters (B = 5.0 Å^2) for the hydrogen atoms of **10b** and **12b** were fixed in calculated positions (C–H, 0.97 Å) during the later cycles of refinement. For structures **6a** and **23**, the positional parameters for the hydrogen atoms, given fixed, arbitrary thermal parameters (B = 5.0 Å^2), were located from a difference Fourier electron density map and were refined.

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Registry No. 4, 15599-91-4; **5**, 14700-00-6; **6a**, 84462-63-5; **6b**, 89178-99-4; **7**, 84462-68-0; **8a**, 84462-64-6; **8b**, 89179-00-0; **9a**, 89179-01-1; **9b**, 89179-02-2; **10a**, 89179-03-3; **10b**, 89179-04-4; **11**, 89179-05-5; **12a**, 89179-06-6; **12b**, 89179-17-7; **13a**, 89179-08-8; **13b**, 89179-09-9; **14a**, 84462-65-7; **14b**, 89196-42-9; **15**, 84462-67-9; **16**, 940-71-6; **17**, 2950-45-0; **18a**, 88644-58-0; **18b**, 89179-10-2; **19a**, 88656-94-4; **19b**, 89179-11-3; **20**, 89179-12-4; **21a**, 89196-43-0; **21b**, 89196-44-1; **22a**, 89196-45-2; **22b**, 89196-46-3; **23**, 89196-47-4; **24**, 77589-25-4; **25a**, 89179-13-5; **25b**, 89179-14-6; **28**, 89196-48-5; **29**, 89179-15-7; **30**, 89179-16-8; $Fe(\eta\text{-}C_5H_5)_2$, 102-54-5; $Li(n\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$, 1271-15-4; $Br(n\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$, 1273-73-0; $ClHg(n\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$, 1273-75-2; $Ru(\eta\text{-}C_5H_5)_2$, 1287-13-4; $Li(n\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$, 89179-17-9; $Li_2(n\text{-}C_5H_4)_2Ru$, 60898-13-7; $Br(n\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$, 38816-65-8; $N_3P_3F_4(OCH_2CH_3)(n\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$, 89178-97-2; $N_3P_3F_3(OCH_2CH_3)_2(n\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$, 89178-98-3; $Li_2(n\text{-}C_5H_4)_2Fe$, 33272-09-2; $NaOCH_2CF_3$, 420-87-1; CH_3I, 74-88-4; $Cl(n\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)$, 1273-74-1; $Cl(n\text{-}C_5H_4)Ru(\eta\text{-}C_5H_5)$, 38959-07-8; $LiEt_3BH$, 22560-16-3.

Supplementary Material Available: Includes the positional and thermal parameters from the final cycles of refinement (Tables VI, X, XIV, and XVIII), a list of interatomic distances and bond angles for the four compounds (Tables VII, XI, XV, and XIX), tables of least-squares planes (Tables VIII, XII, XVI, and XX), and calculated structure factors (Tables IX, XIII, XVII, and XXI) (64 pages). Ordering information is given on any current masthead page.

Anionic Alkyne Complexes of Tungsten

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Abstract: Anionic tungsten complexes have been prepared in which the ligand environment is dominated by alkyne ligands. Reduction of $[W(PhC{\equiv}CPh)_3CO]$ with lithium naphthalenide leads to formation of an anionic complex suggested to be $[W(PhC{\equiv}CPh)_3]^{2-}$, the first homoleptic anionic alkyne complex of a transition metal. The dianion has been characterized chemically by derivatization with Ph_3SnCl to form $[W(PhC{\equiv}CPh)_3SnPh_3]^-$, isolated as $[W(PhC{\equiv}CPh)_3SnPh_3]NEt_4$ (**2**) and structurally characterized by a single-crystal X-ray diffraction study. The acetylenic carbons form a tapered triagonal-prismatic coordination sphere for the W, with the Ph_3Sn ligand capping a trigonal face. Dynamic ^{13}C NMR studies have shown that **2** undergoes a rapid fluxional process, with a free energy of activation of 13.0 kcal mol^{-1} at room temperature, which is suggested to involve rotation of the alkyne ligands.

It has been recognized for many years that the reactions of anionic organotransition-metal complexes with electrophiles provide convenient routes to a wide variety of other molecules, but until recently the ligand environment in most common anionic systems has included the strongly π-acidic carbonyl ligand and was frequently dominated by this ligand. Typical examples of such carbonyl metalates include $[Fe(CO)_4]^{2-}$,[1,2] the group 6A carbonyl dianions $[M(CO)_5]^{2-}$,[1,3] $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]^-$,[1] and $[M(\eta^5\text{-}C_5H_5)(CO)_3]^-$ (M = Cr, Mo, W).[1] Jonas and co-workers,[4]

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however, have now established the existence of an extensive chemistry of anionic late transition-metal complexes in which the ligands are primarily alkenes, and this work suggests that versatile anionic intermediates may be accessible in a much wider range of systems than had previously been assumed. Since the preparation of such intermediates could lead to rapid development of the chemistry of the ligand environments involved, we have recently explored the application of alkali naphthalenide reduction of substrates that can lose a donor ligand to the preparation of anionic complexes that do not contain carbonyl ligands. The present paper reports the application of this reaction to the reduction of $[W(PhC{\equiv}CPh)_3CO]$.

The unusual polyalkyne complexes $[W(RC{\equiv}CR')_3CO]$ ($R + R' = 2Ph, 2C_2H_5$, and $CH_3 + Ph$) were first reported by Tate and Augl in 1963[5a] and provide the classic examples of molecules in which nonbridging alkyne ligands use the electrons in both of their π-bonds to bind to a transition-metal atom. This concept led to a symmetry-adapted molecular orbital description of the bonding within the complexes that accounted for their C_{3v} structures[6] in terms of the effective atomic number rule[5] and was later used by King to explain the stoichiometry of the complexes.[8] It was pointed out that the formation of the monocarbonyl complexes, in which the acetylenes contribute 10 electrons to bonding molecular orbitals, in preference to a hypothetical tris-alkyne "$[W(RC{\equiv}CR)_3]$" in which the alkynes contribute all 12 of their π-electrons, is a necessary consequence of symmetry restrictions on the bonding interactions. Subsequent work by Templeton has established that ^{13}C NMR chemical shifts provide a sensitive probe for 4-electron donation from alkyne ligands[9a] and that the average number of electrons contributed to the bonding electron framework by each alkyne in these and a variety of other alkyne complexes correlates well with the chemical shift of the alkyne carbons.[9b]

Experimental Section

General Data, Solvents, and Reagents. All reactions and manipulations were carried out under dry nitrogen by using standard Schlenk-tube techniques or a Vacuum Atmospheres Dri-lab glovebox. All glassware was oven dried or flamed under vacuum before use. Dry tetrahydrofuran (THF) and diethyl ether were freshly distilled from Na/benzophenone ketyl before use. Absolute ethanol was used as received. Acetone was AR grade and used without further purification. $[NEt_4]Br$ was recrystallized from absolute ethanol and dried under 0.1-torr vacuum for 12 h at 60 °C. $[W(PhC{\equiv}CPh)_3CO]$ was prepared by the literature method from $[W(MeCN)_3(CO)_3]$.[5b]

Approximately 0.2 M lithium naphthalenide was prepared by dissolving lithium wire containing 0.02% Na (Alfa Products) in a solution of naphthalene (1.5 equiv) in THF. Considerable care was taken to ensure that the naphthalenide solution was free of basic contaminants by carefully scraping the surface of the wire in the glovebox until it was free of crust. The naphthalenide was standardized by addition of 1-mL aliquots to 10 mL of O_2-free H_2O, which was then titrated with 0.1 M HCl, using phenolphthalein indicator. Naphthalenide solutions were checked for residual base by a procedure in which 1-mL aliquots were first added to 5 mL of 1,2-dibromoethane. This was then stirred with 5 mL of O_2-free H_2O, and the biphasic system was titrated with 0.1 M HCl to determine the residual base. This was typically below 10^{-3} M and solutions with levels higher than 10^{-3} M were discarded.

IR spectra were recorded in THF solution or as mulls in Na-dried mineral oil on a Perkin-Elmer 457 spectrometer. Microanalyses were carried out by Dornis and Kolb, Mulheim a.d. Ruhr, West Germany.

NMR Studies. NMR spectra were recorded on a Bruker WM-300-WB at the following frequencies: ^1H, 300 MHz; ^{13}C, 75.5 MHz; ^{119}Sn, 112 MHz. ^{13}C spectra were recorded in acetone-d_6, methylene-d_2 chloride, or tetrachloroethylene as indicated below and calibrated by using the methyl resonance of the acetone at 29.8 ppm or the CD_2Cl_2 resonance at 53.8 ppm as an internal standard as appropriate. ^{119}Sn spectra were recorded in acetone-d_6 at 302 K, and chemical shifts are reported in terms of the absolute frequency Ξ[10a] and calculated relative to $\Xi(Me_4Sn) = 37.290665$ MHz.[10b] ^1H NMR spectra were calibrated by using the CHD_2COCD_3 resonance in the solvent at δ 2.04 as an internal standard.

Table I. Crystal Data[16] for $[W(PhC{\equiv}CPh)_3SnPh_3]NEt_4$

T, K	$\approx$300	β, deg	111.07 (2)
space group	$P2_1/n$ (No. 14)	V, Å^3	5593 (2)
a, Å	19.655 (5)	D_c, g cm^{-3}	1.42
b, Å	12.662 (3)	μ, cm^{-1}	25.87
c, Å	24.084 (7)	Z	4

Probe temperatures recorded during dynamic NMR studies were calibrated by using the temperature dependence of the difference in chemical shift between the ^1H resonances of the CH_3 and OH groups of methanol below ambient temperatures and between the ^1H resonances of the CH_2 and OH groups of ethylene glycol above ambient temperatures.[11] Exchange rates were calculated from coalescence temperatures by means of the approximate relationship[12]

$$2\pi\tau(\Delta\nu) = 2^{1/2}$$

This relates the difference in chemical shift $\Delta\nu$ between two equally populated exchanging sites to a lifetime τ, which is half the lifetime of either site at the coalescence temperature. The expression is derived for the situation in which there is no coupling between the sites, as is the case for all the coalescing absorptions in the present experiment, and under these conditions provides exchange rates which compare favorably with those calculated from full line shape analysis provided $\Delta\nu > 4$ Hz.[13] The difference in chemical shifts at the coalescence temperature was assumed to be unchanged from that at 213 K for the ipso, ortho, meta, and para carbons of the acetylenic phenyls, as indicated by plots of $\Delta\nu$ against T from 213 to 253 K for those resonances. The difference in chemical shift at the coalescence temperature for the acetylenic carbons was calculated from the 213 K value on the assumption that the small temperature dependence observed in the range 213–253 K could be extrapolated linearly to T_c. Values for the free energy of activation at the coalescence temperature were obtained from the exchange rate by application of the Eyring equation.[14] The transmission coefficient κ was assumed to equal unity, as is usual in dynamic NMR studies.[15]

$[W(PhC{\equiv}CPh)_3SnPh_3]NEt_4$. A magnetically stirred THF solution of $[W(PhC{\equiv}CPh)_3CO]$ (3.07 g, 4.11 mmol in 50 mL) was cooled to −78 °C and 68.5 mL of a 0.12 M solution of lithium naphthalenide in THF (2.0 equiv) was syringed in dropwise over 5 min. A very intense red-purple color developed immediately. After 5 min of stirring, a THF solution of Ph_3SnCl (2.07 g, 4.11 mmol in 80 mL), precooled to −78 °C, was added over a period of 10 min by using a 20-gauge stainless steel cannula to run the solution down the inside wall of the cooled vessel. After addition was complete, the solution was removed from the cold bath and allowed to warm to room temperature. During this process the red color decreased markedly in intensity, but no further changes were observed while the solution stirred for 1 h at room temperature. The solvent was then removed under vacuum to leave an oily brown residue, which was washed with toluene (3 × 20 mL) to give the lithium salt of $[W(PhC{\equiv}CPh)_3SnPh_3]^-$ (2.15 g, 1.95 mmol, 47%) as a pale tan solid, which was collected by filtration and dried under vacuum for 3 h.

In a typical counterion exchange, 1.42 g (1.32 mmol) of this material was dissolved in the minimum volume of EtOH and treated with a twofold excess of a saturated solution of anhydrous $[NEt_4]Br$ in EtOH to give an ivory precipitate, which was collected by filtration and washed with 10 mL of H_2O. After drying under vacuum for 3 h, this gave 1.03 g (0.86 mmol, 65%, 31% overall from $[W(PhC{\equiv}CPh)_3CO]$) of spectroscopically pure $[W(PhC{\equiv}CPh)_3SnPh_3]NEt_4$ (^1H NMR). Analytical

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Table II. Atomic Fractional Coordinates (×10^4) for [W(PhC≡CPh)$_3$SnPh$_3$]NEt$_4$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
W	4077 (1)	300 (1)	1719 (1)	C_{73}	4336 (5)	-2867 (7)	3949 (3)	H_{52}	4890	-1152	335
Sn	4840 (1)	-239 (1)	2912 (1)	C_{74}	4706 (5)	-3714 (7)	3863 (4)	H_{53}	4535	-1298	-705
C_1	3124 (3)	69 (5)	1879 (3)	C_{75}	5141 (5)	-3595 (7)	3532 (4)	H_{54}	3342	-900	-1318
C_{11}	2664 (4)	-309 (6)	2222 (3)	C_{76}	5187 (4)	-2639 (6)	3280 (3)	H_{55}	2519	-292	-911
C_{12}	2021 (4)	174 (7)	2170 (3)	C_{81}	6039 (4)	-56 (6)	3232 (3)	H_{56}	2859	-169	130
C_{13}	1564 (4)	-222 (8)	2451 (4)	C_{82}	6463 (4)	-689 (8)	3030 (4)	H_{62}	5828	-1332	1370
C_{14}	1775 (5)	-1134 (8)	2800 (4)	C_{83}	7213 (5)	-579 (10)	3217 (4)	H_{63}	6588	-2826	1630
C_{15}	2409 (5)	-1614 (7)	2858 (4)	C_{84}	7539 (5)	230 (9)	3598 (4)	H_{64}	6225	-4310	1995
C_{16}	2851 (4)	-1212 (6)	2565 (3)	C_{85}	7135 (4)	868 (8)	3799 (4)	H_{65}	5109	-4376	2118
C_2	2962 (3)	482 (5)	1353 (3)	C_{86}	6394 (4)	739 (7)	3621 (3)	H_{66}	4373	-2848	1928
C_{21}	2316 (3)	710 (5)	822 (3)	C_{91}	4625 (4)	827 (6)	3544 (3)	H_{72}	4113	-1314	3763
C_{22}	2272 (4)	1579 (6)	466 (3)	C_{92}	4958 (4)	701 (7)	4157 (3)	H_{73}	4039	-2936	4188
C_{23}	1685 (5)	1716 (7)	-64 (3)	C_{93}	4904 (5)	1468 (8)	4549 (4)	H_{74}	4665	-4387	4031
C_{24}	1132 (4)	988 (8)	-241 (3)	C_{94}	4512 (5)	2364 (8)	4345 (5)	H_{75}	5416	-4186	3476
C_{25}	1159 (4)	138 (7)	108 (3)	C_{95}	4176 (5)	2490 (7)	3755 (5)	H_{76}	5493	-2579	3047
C_{26}	1738 (4)	-13 (5)	643 (3)	C_{96}	4209 (4)	1750 (6)	3356 (4)	H_{82}	6232	-1231	2746
C_3	4308 (4)	1722 (5)	1415 (3)	N	7506 (4)	3728 (5)	-384 (3)	H_{83}	7500	-1059	3083
C_{31}	4265 (4)	2488 (5)	945 (3)	C_{1N}	7092 (7)	4142 (10)	-17 (7)	H_{84}	8055	339	3721
C_{32}	4572 (5)	3480 (7)	1075 (4)	C_{2N}	6482 (7)	3440 (9)	22 (6)	H_{85}	7368	1426	4071
C_{33}	4594 (6)	4169 (9)	630 (4)	C_{3N}	7820 (6)	2664 (9)	-184 (6)	H_{86}	6117	1210	3771
C_{34}	4314 (5)	3845 (8)	55 (4)	C_{4N}	8306 (7)	2594 (11)	481 (5)	H_{92}	5232	70	4311
C_{35}	4004 (5)	2887 (7)	-90 (4)	C_{5N}	8124 (7)	4493 (10)	-334 (8)	H_{93}	5145	1365	4969
C_{36}	3970 (4)	2212 (6)	348 (3)	C_{6N}	7927 (8)	5574 (10)	-538 (6)	H_{94}	4475	2895	4618
C_4	4742 (4)	1630 (5)	1970 (3)	C_{7N}	6979 (7)	3624 (12)	-1008 (6)	H_{95}	3904	3126	3609
C_{41}	5393 (4)	2220 (6)	2338 (3)	C_{8N}	7313 (8)	3166 (14)	-1441 (6)	H_{96}	3943	1860	2940
C_{42}	6053 (4)	2025 (7)	2275 (4)	H_{12}	1880	803	1933	H_{1Na}	7434	4249	380
C_{43}	6668 (5)	2590 (9)	2574 (4)	H_{13}	1113	126	2406	H_{1Nb}	6881	4807	-182
C_{44}	6649 (5)	3367 (9)	2942 (5)	H_{14}	1469	-1418	2996	H_{2Na}	6250	3777	264
C_{45}	6014 (6)	3562 (7)	3045 (4)	H_{15}	2557	-2234	3102	H_{2Nb}	6682	2774	197
C_{46}	5393 (5)	3014 (6)	2738 (4)	H_{16}	3296	-1571	2604	H_{2Nc}	6131	3324	-370
C_5	4129 (4)	-500 (5)	994 (3)	H_{22}	2653	2099	586	H_{3Na}	7424	2173	-258
C_{51}	3910 (4)	-625 (6)	334 (3)	H_{23}	1667	2324	-307	H_{3Nb}	8109	2466	-415
C_{52}	4401 (4)	-973 (7)	84 (3)	H_{24}	730	1080	-610	H_{4Na}	8486	1887	574
C_{53}	4190 (5)	-1065 (9)	-532 (4)	H_{25}	770	-370	-17	H_{4Nb}	8024	2781	720
C_{54}	3487 (5)	-823 (9)	-894 (4)	H_{26}	1741	-610	889	H_{4Nc}	8709	3073	562
C_{55}	3005 (5)	-479 (7)	-657 (4)	H_{32}	4776	3702	1482	H_{5Na}	8394	4204	-560
C_{56}	3211 (4)	-393 (6)	-37 (3)	H_{33}	4803	4860	729	H_{5Nb}	8431	4526	79
C_6	4547 (4)	-976 (5)	1473 (3)	H_{34}	4338	4306	-254	H_{6Na}	8361	5974	-484
C_{61}	5011 (4)	-1945 (6)	1615 (3)	H_{35}	3806	2674	-499	H_{6Nb}	7664	5892	-313
C_{62}	5677 (5)	-1944 (8)	1531 (4)	H_{36}	3738	1538	237	H_{6Nc}	7625	5568	-952
C_{63}	6125 (7)	-2834 (12)	1681 (4)	H_{42}	6080	1472	2011	H_{7Na}	6589	3170	-1007
C_{64}	5911 (7)	-3703 (10)	1896 (5)	H_{43}	7116	2426	2520	H_{7Nb}	6789	4313	-1148
C_{65}	5261 (8)	-3742 (8)	1977 (4)	H_{44}	7075	3788	3134	H_{8Na}	6946	3124	-1832
C_{66}	4818 (5)	-2842 (6)	1850 (4)	H_{45}	6008	4084	3333	H_{8Nb}	7500	2472	-1311
C_{71}	4806 (4)	-1751 (5)	3350 (3)	H_{46}	4949	3179	2800	H_{8Nc}	7702	3614	-1451
C_{72}	4383 (4)	-1901 (6)	3696 (3)								

samples were prepared by recrystallization from acetone at -60 °C.

Anal. Calcd for $C_{68}H_{65}NSnW$: C, 68.13; H, 5.47. Found: C, 68.00; H, 5.28. IR (Nujol mull, selected) 1650 cm^{-1} (C≡C); ^{1}H NMR [$(CD_3)_2CO$, 300 MHz] δ 7.2–6.8 (complex, 45 H, Ph), 3.42 (q, 8 H, J = 7.4 Hz, NC*H*$_2$CH$_3$), 1.33 (tt, 12 H, J = 7.3 Hz, $^3J_{^{14}N-H}$ = 1.9 Hz, NCH$_2$C*H*$_3$).

The crystalline solid was light sensitive, changing color to green-blue after more than 1 h of exposure to indirect sunlight. The photodecomposition products could be removed by trituration. During the addition of Ph_3SnCl to the reduced solution, and all subsequent operations, the vessels used were wrapped in foil to minimize exposure to light.

X-ray Diffraction Study. The crystal used for the study was sealed under nitrogen and protected from visible light throughout the data collection. The crystal was approximately octahedral in appearance and 0.25 × 0.25 × 0.3 mm in size. Systematic absences indicated that the space group was $P2_1/n$. The unit cell parameters were determined by a least-squares technique from the setting angles of 12 sets of Friedel pairs using graphite-monochromated Mo K$\bar{\alpha}$ radiation (λ = 0.71069 Å). Cell dimensions and other crystal data are listed in Table I. Intensities of reflections with 3° ≤ 2θ ≤ 52° were measured on a Nicolet R3 diffractometer using a $\theta/2\theta$ scan, with a symmetrical 2θ scan range of 1.8°. Background was measured by stationary counts taken at each end of the scans. Intensities of three reflections monitored every 60 measurements showed an average 6% decrease in I after 227 h of exposure. A linear-decay correlation based on the intensities of these three check reflections was applied to the data.

Lorentz and polarization corrections were applied to the data.[17] A semiempirical absorption correction,[18] applied using Nicolet XTL programs, was based on the ψ scans of 12 reflections (with 3° ≤ 2θ ≤ 52°). Atomic scattering factors were based on literature values for W[19] and on those in the SHELXTL program for other atoms. Of the 11413 reflections measured, 7949 independent observed reflections ($F_o > 3\sigma(F_o)$) were included in subsequent calculations.

A three-dimensional Patterson synthesis revealed the position of the W atom. Subsequent Fourier and difference syntheses, using phases derived from the W position, revealed all non-hydrogen atom positions. Hydrogen atoms were placed in calculated positions in the phenyl rings and the ethyl groups (C–H = 0.96 Å). Block-diagonal least-squares refinement based on F with anisotropic thermal parameters assigned to all non-hydrogen atoms and fixed isotropic thermal parameters assigned to H (1.2 × equivalent thermal parameter for the adjacent C atom) converged to $R(F) = 0.0498$, with $R_w(F) = 0.0469$.[20] Weights were taken as $w = [\sigma^2(F) + gF^2]^{-1}$, with $g = 0.0009$.

A final difference Fourier map revealed four peaks (0.7–0.8 e$^-$/Å^3) near W, and random features ≤0.4–0.5 e$^-$/Å^3. A weighting scheme analysis revealed no systematic dependence of $w\Delta F^2$ on $|F_o|$, $(\sin\theta)/\lambda$, or parity of indices. Final atomic positional parameters are presented

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(16) Estimated standard deviations, here and throughout this paper, are given in parentheses in terms of the last digit.

(17) The polarization term for the monochromator was assumed to be midway between that for a perfect and ideally imperfect crystal.

(18) Nicolet XTL Structure Determination Manual, "TAPER". μ = 25.87 cm^{-1}.

(19) "International Tables for X-ray Crystallography"; Ibers, J., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72–98.

(20) $R(F) = \sum|F_o - |F_c||/\sum F_o$; $R_w(F) = \sum|F_o - F_c|w^{1/2}/\sum F_o w^{1/2}$

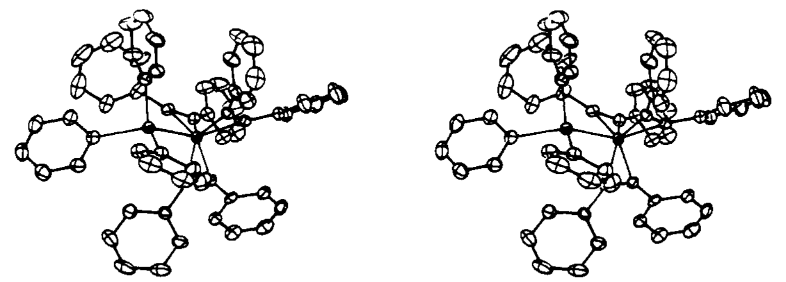

Figure 1. Stereoview of the $[W(PhC{\equiv}CPh)_3SnPh_3]^-$ anion (35% probability ellipsoids, H atoms omitted for clarity).

Table III. Selected Intramolecular Distances (Å) and Angles (Deg) in $[W(PhC{\equiv}CPh)_3SnPh_3]NEt_4$[a]

bond	Å	bond	Å	bond	Å	angle	deg	angle	deg	angle	deg
$W-C_1$	2.065 (7)	$W-C_4$	2.084 (6)	$W-C_6$	2.051 (7)	$C_{11}-C_1-C_2$	132.6 (6)	$C_{41}-C_4-C_3$	132.6 (7)	$C_{61}-C_6-C_5$	136.4 (7)
$W-C_2$	2.061 (6)	$W-C_3$	2.055 (7)	$W-C_5$	2.052 (7)	$C_{21}-C_2-C_1$	139.5 (7)	$C_{31}-C_3-C_4$	133.0 (6)	$C_{51}-C_5-C_6$	137.9 (7)
C_1-C_2	1.300 (9)	C_4-C_3	1.307 (8)	C_6-C_5	1.299 (8)	C_1-W-C_2	36.7 (3)	C_4-W-C_3	36.8 (2)	C_6-W-C_5	36.9 (2)
C_1-C_{11}	1.504 (11)	C_4-C_{41}	1.472 (9)	C_6-C_{61}	1.493 (10)	C_1-W-C_4	125.2 (3)	C_4-W-C_6	114.9 (3)	C_6-W-C_1	118.4 (3)
C_2-C_{21}	1.471 (8)	C_3-C_{31}	1.470 (10)	C_5-C_{51}	1.499 (9)	C_2-W-C_3	95.0 (2)	C_3-W-C_5	92.6 (3)	C_5-W-C_2	93.6 (3)
		W-Sn	2.807 (1)			$W-Sn-C_{71}$	127.2 (2)	$W-Sn-C_{81}$	116.2 (2)	$W-Sn-C_{91}$	113.4 (2)
$Sn-C_{71}$	2.197 (7)	$Sn-C_{81}$	2.212 (7)	$Sn-C_{91}$	2.185 (8)	$C_{71}-Sn-C_{81}$	97.9 (3)	$C_{81}-Sn-C_{91}$	98.1 (3)	$C_{91}-Sn-C_{71}$	99.1 (3)
$N-C_{1N}$	1.50 (2)	$N-C_{3N}$	1.49 (1)	$N-C_{5N}$	1.52 (2)						
$N-C_{7N}$	1.49 (1)	$C_{1N}-C_{2N}$	1.52 (2)	$C_{3N}-C_{4N}$	1.54 (2)						
$C_{5N}-C_{6N}$	1.50 (2)	$C_{7N}-C_{8N}$	1.53 (2)								

[a] All of the phenyl rings in the structure are regular with a maximum deviation from planarity of 0.0235 Å for C_{44}. The average C–C bond length in rings is 1.38 Å, with all C–C bond lengths within 3σ of the mean.

in Table II and thermal parameters are given in Table SII of the supplementary material.

Results and Discussion

Reduction of $[W(PhC{\equiv}CPh)_3CO]$ and Preparation of $[W(PhC{\equiv}CPh)_3SnPh_3]NEt_4$. Reduction of $[W(PhC{\equiv}CPh)_3CO]$ (**1**) with lithium naphthalenide in tetrahydrofuran (THF) proceeds smoothly at −78 °C with concomitant production of an exceptionally intense red-purple color. The reaction was monitored by examining the IR spectrum of aliquots of the mixture and was judged to be complete after addition of 2.0 equiv of naphthalenide when the CO stretching absorption of the starting material could no longer be observed at 2070 cm^{-1}. The color of the solution did not change appreciably when the material was warmed to room temperature, but no tractable products could be isolated from this solution.

The absorption of 2 equiv of naphthalenide in the reduction, together with the loss of the CO stretching absorption of the starting material, suggested that reduction had given the homoleptic dianion $[W(PhC{\equiv}CPh)_3]^{2-}$ (eq 1). This would constitute the first example of a homoleptic anionic alkyne complex, and its preparation would demonstrate that alkynes are quite flexible donor–acceptor ligands and are sufficiently good π-acceptors to stabilize anionic complexes.

The formation of the putative dianion was supported by treatment with Ph_3SnCl, which Ellis has demonstrated to be a valuable reagent for preparing tractable derivatives of highly reduced organometallic species.[3c,21] Addition of a THF solution of Ph_3SnCl to the reduced solution at −78 °C did not result in immediate signs of reaction, but when the solution was warmed to room temperature the intense red-purple color lightened until the solution was a translucent red. Removal of the solvent gave an oily residue from which a white solid could be isolated after cation exchange with $[NEt_4]Br$. The solid could be recrystallized from CH_2Cl_2/diethyl ether as a CH_2Cl_2 solvate, from acetone/diethyl ether as a diethyl ether solvate (^1H NMR), or, with lower mass recovery, from acetone as analytically pure $[W(PhC{\equiv}CPh)_3SnPh_3]NEt_4$ (**2**). The compound was characterized by microanalysis and by a single-crystal X-ray diffraction study.

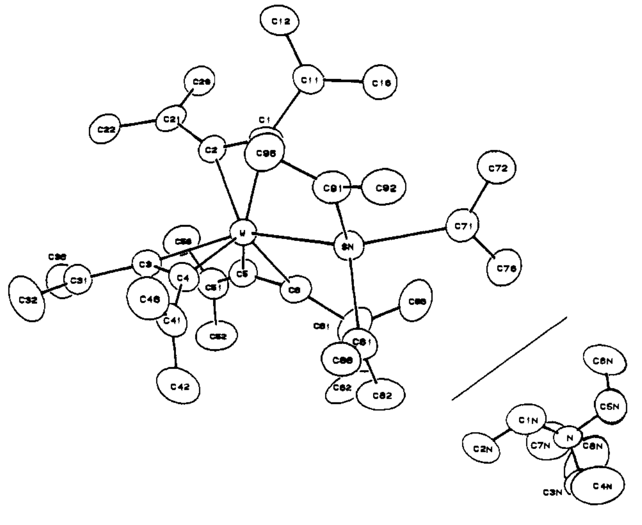

Figure 2. Carbon atom numbering scheme for $[W(PhC{\equiv}CPh)_3SnPh_3]NEt_4$. Hydrogen atoms are given the same number as the carbon atom to which they are bonded, and C and H atoms in the cation are distinguished by a subscript N. Within the cation, the different hydrogens of methylene and methyl groups are distinguished by subscripts a, b, and c.

The isolation of **2** from the reaction of the reduced solution with Ph_3SnCl does not conclusively prove the formation of $[W(PhC{\equiv}CPh)_3]^{2-}$ since Ellis, for example, has reported[3c] that $[W(CO)_5SnPh_3]^-$ can be formed from the reaction of Ph_3SnCl either with $[W(CO)_5]^{2-}$ or its first oxidation product, $[W_2(CO)_{10}]^{2-}$. This raises the possibility that the reduced solution contains a dimeric anion such as $[W_2(PhC{\equiv}CPh)_6]^{2-}$, which could be formulated with bridging acetylenic ligands, rather than the simple monomeric dianion. In view, however, of the stoichiometry of the reduction and the IR evidence for the complete loss of the carbonyl absorption of the staring material, it seems probable that the reduction product is the obvious candidate $[W(PhC{\equiv}CPh)_3]^{2-}$ and that derivatization of this with Ph_3SnCl gives **2** as shown in eq 1.

$$\underset{\mathbf{1}}{[W(PhC{\equiv}CPh)_3CO]} \xrightarrow[-CO]{LiC_{10}H_8} \text{“}[W(PhC{\equiv}CPh)_3]^{2-}\text{”}$$

$$\xrightarrow[(2)\ [NEt_4]Br]{(1)\ Ph_3SnCl} \underset{\mathbf{2}}{[W(PhC{\equiv}CPh)_3SnPh_3]NEt_4} \quad (1)$$

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(21) (a) Chen, Y.-S.; Ellis, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 1141. (b) Ellis, J. E.; Fjare, K. L.; Hayes, T. G. *Ibid.* **1981**, *103*, 6100. (c) Ellis, J. E.; Parnell, C. P.; Hagen, G. P. *Ibid.* **1978**, *100*, 3605. (d) Ellis, J. E.; Barger, P. T.; Winzenburg, M. L. *J. Chem. Soc., Chem. Commun.* **1977**, 686. (e) Ellis, J. E.; Faltynek, R. A.; Hentges, S. G. *J. Organomet. Chem.* **1976**, *120*, 389. (f) Ellis, J. E.; Faltynek, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 1801.

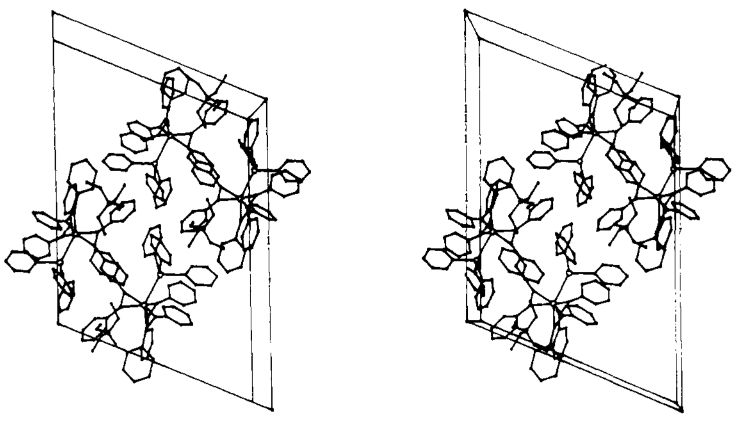

Figure 3. Stereoview of the unit cell of $[W(PhC{\equiv}CPh)_3]NEt_4$ (H atoms omitted for clarity).

Table IV. Comparison of Structural Parameters for 1 and 2

	$[W(PhC{\equiv}CPh)_3CO]$[7]	$[W(PhC{\equiv}CPh)_3SnPh_3]NEt_4$
av W–C_{alkyne}, Å	2.06	2.06 (range 2.05–2.08)
av C≡C, Å	1.30	1.30 (range 1.30–1.31)
av C_{alkyne}–C_i (C_i = ipso C of C_6H_5), Å	1.46	1.48 (range 1.47–1.50)
av C_{alkyne}–C_{alkyne}–C_i, deg	139.6	135.3 (range 132.6–139.5)
av edge of triangle defined by upper end of alkyne, Å	3.56	3.57 (range 3.48–3.68)
av edge of triangle defined by lower end of alkyne, Å	3.08	3.00 (range 2.97–3.03)

X-ray Diffraction Study of $[W(PhC{\equiv}CPh)_3SnPh_3]NEt_4$. The structural analysis, carried out as discussed in the Experimental Section, established that the tungsten anion has the molecular structure shown in Figure 1. The atomic nomenclature is indicated in Figure 2. Selected bond lengths and angles are listed in Table III. The unit cell packing diagram is shown in Figure 3.

The immediate coordination sphere of the tungsten is similar to that in **1**[7] and approximates a tapered trigonal prism, defined by the C atoms of the acetylenes, which is capped on the larger trigonal face by the $SnPh_3$ ligand. The degree of tapering is marked, as indicated by angles of 18° (C_2–C_1), 11° (C_3–C_4), and 17° (C_5–C_6) between the C≡C axes of the acetylenes and the W–Sn vector. For two of the acetylenes this does not give rise to significant differences between the upper and lower W–C distances since the W atom is not centrally located within the prism, being 1.107 Å above the smaller trigonal face and 0.150 Å below the larger trigonal face. The remaining acetylene, that defined by C_3 and C_4, has crystallographically distinct W–C distances of 2.055 (7) and 2.084 (6) Å, but this difference (0.029 (9) Å) is barely significant. Notably, though, the C_3–C_4 acetylene is also unique in the following ways: bending back of the phenyl rings from the alkyne C≡C axis is most severe for this ligand (see Table III), and the phenyl ring containing C_{41}–C_{46} is nearly parallel to the Sn–Ph group containing C_{81}–C_{86}, with a separation close to the van der Waals contact distance ($C_{42}\cdots C_{86}$ = 3.47 Å; see Figures 2 and 3). There is no other discernible pattern in the orientations of the phenyl rings of the acetylene ligands and the triphenyltin ligand, which presumably minimize unfavorable nonbonding interactions in the crystal. These variations in orientation and the associated nonbonding interactions are probably responsible for the deviations of the arrangement of the core atoms of the anion from overall C_{3v} symmetry (see Figure 4). It is unlikely that the distortions are due to any intrinsic electronic difference between the bonding modes of the three acetylenes: although the bonding in **1** and **2** can be thought of as involving two 4-electron and one 2-electron alkyne ligands, the actual electronic structure should correspond to a resonance hybrid involving canonical forms in which all three of the alkynes act as the 2-electron donor. The equivalence of the alkynes can be clearly seen in the MO description of the electronic structure of **2**, which is qualitatively identical with that for **1**[5b] and which would place the two nonbonding alkyne π-electrons in an A_2 symmetry combination of alkyne π-orbitals which has no metal character since none of the metal valence orbitals transforms as A_2 under C_{3v}.

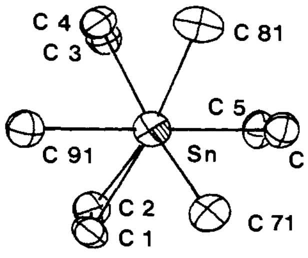

Figure 4. Distortion of inner coordination sphere of W atom from C_{3v} symmetry as seen by viewing anion down Sn–W axis.

A detailed comparison of the structure of **2** with that of **1** is not possible, since only a preliminary communication has appeared on the latter.[7] From the data that are available, however, the structures appear to be remarkably similar, as can be seen by inspection of Table IV. The W–C bonding distances and the C≡C bond lengths are indistinguishable, and the only noteworthy difference is that the phenyl groups in **2** are bent further back from the alkyne C≡C axes. The average value of 135.3° (range 132.6–139.5°) for the C_{alkyne}–C_{alkyne}–C_i angle is the smallest reported for a nonbridging diphenylacetylene (reported range 136–153°),[22] a probable reflection of the steric crowding in the molecule.

The C≡C and M–C_{alkyne} bond lengths within **1** and **2** are typical of those found for coordinated alkynes.[22] A number of groups have considered the possibility that structural data such as these could provide criteria on which to distinguish between 4-electron and 2-electron alkyne ligands[22,23] and examination of the structural data collected for diphenylacetylene complexes in Table V of ref 22 does indicate that the average C≡C length for a 2-electron alkyne (1.279 Å) is shorter than the average C≡C length for a 4-electron alkyne (1.312 Å), while the M–C_{alkyne} distance for a 2-electron alkyne is typically larger than that for a 4-electron alkyne. These differences are, however, comparable to or less than

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(22) Capelle, B.; Dartiguenave, M.; Dartiguenave, Y.; Beauchamp, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 4662 and references therein.

(23) (a) Ricard, L.; Weiss, R.; Newton, W. E.; Chen, J.-J. G.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318. (b) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2352. (c) Robison, E. A. *J. Chem. Soc., Dalton Trans.* **1981**, 2373. (d) Allen, S. R.; Baker, P. K.; Barnes, S. G.; Green, M.; Trollope, L.; Manojlovic-Muir, L.; Muir, K. W. *Ibid.* **1981**, 873.

Table V. $^{13}C\{^1H\}$ NMR Assignments[a,b]

			*Ph*C≡CPh				Sn*Ph*			
	*C*O	Ph*C*≡CPh	ipso	ortho	meta	para	ipso	ortho	meta	para
2 at 305 K in $(CD_3)_2CO$		ca. 192[e]	147.8 s[e]	129.0 d, c	127.8 d, d	125.7 d, t	157.8 s, s[c]	139.8 d, t[c]	126.8 d, d[c]	125.3 d, t
2 at 213 K in $(CD_3)_2CO$		197.3 s[c]	148.3 s, c[c]	129.4 d, t	128.0 d, c	126.7 d, o	157.6 s, c[c]	139.2 d, t[c]	126.8 d, o[c]	125.3 d, o
		183.3 s[c]	145.0 s, t[c]	128.2 d, c	127.7 d, c	125.4 d, o				
1 at 297 K in CD_2Cl_2[d]	219.6 s	192.5 s, t[c]	141.2 s, c	129.8 d, c	129.0 d, d	128.5 d, o				
		174.4 s, t[c]	139.8 s, t[c]	128.6 d, t	128.5 d, o	128.3 d, t				

[a] Absorptions assigned to the solvent and to NEt_4^+ have been omitted from the table. [b] Multiplicities, as observed in coupled or gated decoupled spectra, are indicated by two letters after the peak position. The first indicates the presence (d) or absence (s) of single-bond ^1H coupling, and the second indicates the effect of long-range coupling on the components of the peaks. The letter c indicates unresolved long-range coupling, while the letter o indicates that the long-range coupling pattern cannot be identified because absorptions with similar shifts overlap in coupled spectra. [c] Satellites due to ^{183}W, ^{117}Sn, or ^{119}Sn coupling observed in $^{13}C\{^1H_{bb}\}$ spectra. [d] Multiplicities taken from $CDCl_3$ spectrum at 299 K on a JEOL FX90 at 67.8 MHz. [e] Broadened by exchange effects.

the standard deviations within the data sets and clearly do not provide criteria on which to base distinctions between the bonding modes.

NMR Studies of [W(PhC≡CPh)$_3$CO] and [W(PhC≡CPh)$_3$SnPh$_3$]$^-$: Evidence for Alkyne Rotation within the Complexes. The solid-state structures of **1** and **2** would lead us to anticipate that the ends of the alkynes are in distinct chemical environments in both species, and this has been confirmed for [W(PhC≡CPh)$_3$CO] by ^1H NMR[5] and ^{13}C NMR[9b] data. Since [W(PhC≡CPh)$_3$SnPh$_3$]$^-$ has a very similar geometry and at first appears to be more sterically congested and hence probably less flexible, we were surprised to discover that **2** was fluxional on the ^1H NMR time scale and that room-temperature spectra did not show distinct absorptions for the ortho hydrogens at the two ends of the alkyne.[5b] Dynamic NMR studies at 300 MHz showed that limiting ^1H spectra could be obtained at ≈220 and 368 K, but since the complex coupling within the phenyl groups complicated quantitative analysis, ^{13}C NMR was used for subsequent dynamic studies.

Room-temperature $^{13}C\{^1H\}$ NMR spectra of **2** were relatively simple, but initial assignments were hampered by the apparent absence of resonances corresponding to the acetylenic carbons of the alkyne ligands at the positions predicted by literature correlations (≈180 ppm).[9b] At 213 K, however, two distinct resonances could be seen at 197.3 and 183.3 ppm, and comparison with gated decoupled spectra confirmed their assignment to the acetylenic carbons. With knowledge of these chemical shifts, a single broad acetylene absorption could than be detected at 305 K by inspection of integrated spectra.

The $^{13}C\{^1H\}$ spectrum at 213 K is more complex than the 305 K spectrum and shows 14 different resonances that can be assigned to the [W(PhC≡CPh)$_3$SnPh$_3$]$^-$ anion, as expected if the acetylenic ligands are identical but their ends are distinct. The resonances assignable to the alkyne ligands were readily distinguished since they form two distinct sets which coalesce in pairs as the sample is warmed. The ipso carbons of both alkyne and tin phenyls were identified by the absence of single-bond hydrogen coupling from gated decoupled spectra, and the para carbons were identified by examination of integrated spectra. The distinction between meta and ortho absorptions was based on the (limited) long-range coupling[24] resolved in both 213 and 305 K gated spectra, which also supported some of the other assignments.[24] The assignments and coupling patterns at 213 and 305 K are recorded in Table V. All assignments are consistent with the integrals of the peaks after allowing for NOE effects.

Coalescence temperatures (T_c) were determined for all the chemically inequivalent alkyne carbons by inspection of spectra recorded at 5 K intervals and were used to calculate exchange rates and free energies of activation (Experimental Section and Table VI). Since the temperatures covered a range of about 50 K an attempt was made to determine $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, but linear regression gave a correlation coefficient of only 0.6, reflecting the imprecision in determining T_c. The most that can be said with confidence is that $\Delta G^{\ddagger}$ does not have a marked temperature dependence and that $\Delta S^{\ddagger}$ for the fluxional process is probably small.

Table VI. Coalescence Temperatures and Corresponding $\Delta G^{\ddagger}$ for Alkyne Rotation in 2

C of PhC≡CPh	$\Delta\nu$, Hz	T_c, K	$\Delta G^{\ddagger}$, kcal mol^{-1}
acetylenic	1009	302 (3)	13.1
ipso	248	285 (2)	13.1
ortho	92	274 (3)	13.1
meta	19	256 (4)	13.0
para	96	270 (3)	12.9

The small $\Delta S^{\ddagger}$ suggests that an intramolecular process is responsible for fluxionality in [W(PhC≡CPh)$_3$SnPh$_3$]$^-$, and this was confirmed by two NMR experiments. In the first of these, addition of free PhC≡CPh was observed to have a negligible effect on both the line shapes of the coordinated alkyne resonances and their chemical shifts, suggesting that dissociation of the alkyne was unlikely to be occuring on the NMR time scale. In the second experiment the ^{119}Sn spectrum of the anion was recorded and observed to consist of a singlet at Ξ = 37.292799 (see Experimental Section: 57.2 ppm relative to Me_4Sn) with ^{183}W satellites (J = 715 Hz). It seems unlikely that this coupling would be observed if the fluxionality involved reversible loss of the ligand as, for example, a Ph_3Sn^- anion.

The intramolecular process most likely to account for the observed fluxionality is the well-established rotation of an alkyne ligand. The first reported examples involved alkynes bonded to the metal as 2-electron ligands[25] analogous to alkenes, but cases are known in which it can be assumed that the alkyne bonds through both π-orbitals and acts as a 4-electron ligand.[9a,26] The observed barrier of 13.0 kcal mol^{-1} for alkyne rotation in **2** is lower than most of the literature values but does not fall below the known range.[9a]

There does not appear to be any general correlation between the barrier to rotation in alkyne complexes and the bonding mode of the alkyne, and this is dramatically demonstrated by comparison of the barrier to rotation for **2** with that for **1**, which would be expected to have a similar tungsten–alkyne interaction on the basis of the structural similarities. The room-temperature ^{13}C NMR spectrum of **1** (Table V) shows that $\Delta G^{\ddagger}$ is so large, however, that even the para carbons of the phenyl groups of the acetylenes, with a small $\Delta\delta$ of 0.2 ppm in CD_2Cl_2, give rise to distinct resonances. It was only possible to observe coalescence at 342 ± 2 K in the high-boiling solvent tetrachloroethylene, leading to a value for $\Delta G^{\ddagger}$ of 17.8 ± 0.1 kcal mol^{-1}. No other ^{13}C resonances of the

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(24) Ernst, L.; Wray, V.; Chertkov, V. A.; Sergeyev, N. M. *J. Magn. Reson.* **1977**, *25*, 123.

(25) (a) Ashley Smith, J.; Johnson, B. F. G.; Segal, J. A. *J. Organomet. Chem.* **1973**, *49*, C38. (b) Segal, J. A.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1975**, 1990. (c) Herberhold, M.; Alt, H.; Kreiter, C. G. *J. Organomet. Chem.* **1972**, *42*, 413. (d) Herberhold, M.; Alt, H.; Kreiter, C. G. *Justus Liebigs Ann. Chem.* **1976**, 300.

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alkyne were observed to coalesce. ^{13}C assignments for **1** are based on a comparison of ^{13}C{^{1}H} spectra with gated decoupled spectra and are consistent with the $^1J_{CH}$ couplings, with the long-range coupling[24] in gated spectra, and with the relative intensities of the resonances. Chemical shift differences for the aromatic carbons parallel those observed for **2**. The chemical shifts of the acetylenic carbons are similar to those reported for the analogous hexyne complex.[9b]

The absence of obviously unfavorable intramolecular interligand nonbonding interactions in crystalline **2** would argue against the difference in $\Delta G^‡$ for alkyne rotation in **1** and **2** being due to steric factors such as strain relief in **2** and suggests that electronic effects must be considered. The small drop in ν(C≡C) (1650 cm^{-1}, as compared with 1675 cm^{-1} [27] for **1**) suggests that there is increased π-back-donation to ligand π^*-orbitals in the more electron-rich **2**, but the absence of structural differences between **1** and **2** indicates that the ground-state differences are not marked. If, however, π-back-bonding is a more significant component of the alkyne–metal interactions in the transition state for rotation[28] than in the ground state, the higher charge density on the metal in **2** may lead to a lower energy transition state for rotation in **2**.

Conclusion

The reduction of [W(PhC≡CPh)$_3$CO] (**1**) to give what is suggested to be [W(PhC≡CPh)$_3$]$^{2-}$ shows that anionic transition-metal complexes with alkyne ligands may be more readily accessible than had been generally assumed. Subsequent reaction of the intermediate anion with Ph$_3$SnCl confirms that such species will react readily with electrophiles and suggests that they could prove to be useful intermediates in the synthesis of a range of unusual organometallic complexes. Further work is continuing in these laboratories on the development of the chemistry of alkyne complexes of tungsten.

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Registry No. W(PhC≡CPh)$_3$CO, 12120-72-8; [W(PhC≡CPh)$_3$SnPh$_3$]NEt$_4$, 88635-91-0; [W(PhC≡CPh)$_3$SnPh$_3$]Li, 88635-92-1.

Supplementary Material Available: Tables of observed and calculated structure factors and of atomic thermal parameters (28 pages). Ordering information is given on any current masthead page.

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[27] This work.

[28] This transition state would have the geometry of a highly distorted quadrilaterally capped trigonal prism if the potential energy curve for rotation approximates a single maximum function.

Conformations of Saturated Six-Membered Ring Phosphorus Heterocycles. Axial, Nonplanar Dimethylamino Group of 5,5-Dimethyl-2-(dimethylamino)-2-oxo-1,3,2-oxazaphosphorinane As Determined by X-ray Crystallography. ^{1}H NMR and IR Spectroscopic Analysis of Conformation in Solution

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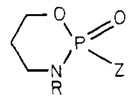
Abstract: The title compound (**7**) crystallized in space group *Pbca* with a = 7.409 (2) Å, b = 12.180 (2) Å, c = 21.912 (4) Å, Z = 8, R = 0.061, R_w = 0.075. The molecule adopts a chair conformation with the 2-dimethylamino substituent axial. The sum of the bond angles about the exocyclic Me$_2$N(2) (349.3 (13)°) shows a considerable deviation from planarity. The exocyclic P-N(2) bond length is unusually long (1.644 (5) Å). The molecules are intermolecularly hydrogen bonded in chains by way of the N(3)H and phosphoryl oxygen. From ^{1}H NMR measurements at 300 MHz along with IR results, it is concluded that the same chair conformation is the predominant one populated in solution, by contrast to the known corresponding 1,3,2-dioxaphosphorinane for which Me$_2$N is equatorial. It is concluded that the dimethylamino group is an effectively smaller substituent (lower axial conformational energy) in the 1,3,2-oxazaphosphorinane ring and in that system is also smaller than the mustard moeity N(CH$_2$CH$_2$Cl)$_2$. Intermolecular hydrogen bonding can play a secondary role in determining conformation. The P-N(2) bond lengthening and pyramidal N(2) are attributed to the nonoptimal conformation about the P-N bond required for the axial Me$_2$N to avoid potential 1,3-syn-axial repulsive steric interactions with the axial hydrogens at C4 and C6.

The 1,3,2-oxazaphosphorinane ring system is of basic interest with regard to an understanding of the effects of heteroatom substitution on the conformational properties of saturated six-membered rings. Moreover, the clinically useful anticancer drugs[2] cyclophosphamide (**1**), isophosphamide (**2**), and trophosphamide (**3**) all contain the 1,3,2-oxazaphosphorinane ring. Cyclophosphamide itself is known to undergo equilibration between alternative chair conformations in solution (**4** ⇄ **5**, Z = N(CH$_2$CH$_2$Cl)$_2$; R = H)[3] however, no systematic study of the effect



1, R = H; Z = N(CH$_2$CH$_2$Cl)$_2$
2, R = CH$_2$CH$_2$Cl; Z = N(CH$_2$CH$_2$Cl)$_2$
3, R = CH$_2$CH$_2$Cl; Z = NHCH$_2$CH$_2$Cl

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