Table I. Vibrational Frequencies (cm^{-1}) for Solid $W(CO)_3(PCy_3)_2(H_2)$ and Isotopically Substituted Species[a]

	HH	HD	DD
ν(HH)	2690 (IR)[b]	2360 (IR)	~1900 (R)
$\nu_a(WH_2)$	1570 (IR)	~1350 (IR)[b]	~1132 (IR)[b]
$\nu_s(WH_2)$	953 (IR, R)	791 (IR, R)	703 (IR, R)
$\delta(WH_2)$	~450 (IR)[b]		319 (IR)

[a] IR samples were Nujol mulls; Raman samples were enclosed in capillaries and excited by the 5682-Å line of a Kr laser. Similar results were obtained for the P-*i*-Pr_3 analogues. [b] Partially obscured. ν(HH) was relatively clear in the $P(C_6D_{11})_3$ analogue.

0.84 Å (neutron, ΔF), slightly larger than that obtained from free H_2 (0.74 Å). The H_2 ligand axis is approximately parallel to the trans phosphorous–phosphorous direction.

Vibrational spectra of solid samples of the H_2, D_2, and HD forms (M = W) are consistent with coordination of molecular H_2. Of the six fundamentals expected from η^2 M–H_2 binding, four are observed (Table I). Bands at 950 and 1570 cm^{-1} have been assigned as symmetric and asymmetric M–H_2 stretches, respectively. Both modes exhibit deuterium isotopic shifts close to those predicted for pure M–H_2 stretching symmetry coordinates. Most importantly, an entirely new set of band positions is observed for the HD complexes, intermediate to those of the H_2 and D_2 species.[10] The H–H stretch is observed at 2690 cm^{-1} in the Nujol mull IR spectrum of $W(CO)_3(PCy_3)_2(H_2)$, while the HD species exhibits a similar broad IR absorption at ca. 2360 cm^{-1}, which we attribute to the H–D stretch. Although the D–D IR stretch was obscured for the D_2 complex, Raman spectra show a weak, broad feature at ca. 1900 cm^{-1}, which we assign to this mode intensified by coupling with the nearby C–O stretches.[11] The deformation and torsional modes of the metal-bound H_2 are more difficult to assign as they are weak or unobserved. However, an IR feature at 319 cm^{-1} for $W(CO)_3(PCy_3)_2(D_2)$ and absent at this frequency for the H_2 species is attributed to an M–D_2 deformation. Also, we note that frequencies of several Raman modes in the 400–600-cm^{-1} region, where M–CO stretch and M–C–O deformations occur, are significantly shifted by deuterium substitution. Three of these modes, including the strongest at 452 cm^{-1}, shift to higher frequency (e.g., 456 cm^{-1}) upon deuteration. We ascribe these unusual deuterium shifts to the presence of M–H_2 deformation modes strongly coupled to the M–CO stretch and M–C–O deformation and stress that metal hydride complexes do not exhibit bands in these low-frequency regions.[12]

The ^1H NMR spectrum of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ under H_2 atmosphere shows a single, broad, temperature- and concentration-independent resonance due to the H_2 ligand at τ 14.21.[13] No coupling to ^{31}P or ^{183}W is resolved in the temperature range +60 to −85 °C. The broad line width (15–40 Hz at half-height) over such a large range may result from exchange and fluxionality involving the H_2 ligand and/or dipolar interaction between the two closely separated hydrogen atoms. The chemical shift is comparable to that found for the hydride ligands in $WH_4(PEt_3)_4$.[14] Unequivocal evidence for direct H–H bonding is provided by the ^1H spectrum of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(HD)$,[15] which shows splitting of the signal at τ 14.2 by spin 1 deuterium into a 1:1:1 triplet with J_{HD} = 33.5 Hz. This value is an order of magnitude larger than that found for compounds containing nonbonded H and D atoms and can be compared to that for HD gas, 43.2 Hz.[16] Since the observed coupling does not vary significantly with the amount of excess HD present, we conclude that it indeed represents J_{HD} for the coordinated HD and reflects a decreased H–D bond order relative to free HD. The line width of the HD resonances is considerably less broad (8 Hz at 35 °C) than that for the H_2 signal (24 Hz), consistent with reduced dipolar broadening. $^{31}P\{^1H\}$ NMR of $W(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$ shows a single resonance with ^{183}W satellites.[13] No coupling to the H_2 protons is resolved at 35 °C in the ^{31}P spectrum.

The H_2 complexes are significant in that they may represent an arrested form of oxidative addition of H_2 to metals. Low-temperature neutron diffraction experiments, using continuous as well as pulsed sources, are currently under way to obtain more meaningful structural parameters and will be the subject of future publications.

Acknowledgment. This work was performed under the auspices of the Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences. We thank Dr. Russell S. Drago for suggesting the NMR study of the HD complex and Dr. Robert E. London for helpful discussions concerning NMR data.

Registry No. $Mo(CO)_3(PCy_3)_2$, 73690-53-6; $W(CO)_3(PCy_3)_2$, 73690-56-9; *mer-trans*-$Mo(CO)_3(PCy_3)_2(H_2)$, 88211-52-3; *mer-trans*-$W(CO)_3(PCy_3)_2(H_2)$, 88211-53-4; $Mo(CO)_3(P\text{-}i\text{-}Pr_3)_2(H_2)$, 88211-54-5; $W(CO)_3(p\text{-}i\text{-}Pr_3)_2(H_2)$, 88211-55-6; $Mo(CO)_3(P\text{-}i\text{-}Pr_3)_2$, 88211-56-7; $W(CO)_3(P\text{-}i\text{-}Pr_3)_2$, 88211-57-8.

Supplementary Material Available: Tables of positional and thermal parameters, interatomic distances and angles, least-squares planes, and observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

(10) In conrast, see: Eberhardt, G. G.; Vaska, L. *J. Catal.* **1967**, *8*, 183.
(11) ν_{CO} = 1962.3, 1857.0 cm^{-1} for $W(CO)_3(PCy_3)_2(H_2)$; 1962.8, 1847.0 cm^{-1} for the D_2 species.
(12) For metal hydride complexes, δ_{MH} generally occurs in the region 700–900 cm^{-1}. Rare-gas matrix-isolated hydrides of the type FeH_2 have recently been described (Ozin, G. A.; McCaffrey, J. G.; McIntosh, D. F. *J. Pure Appl. Chem.*, in press) and found to exhibit IR bands in the 300–400-cm^{-1} region. Preliminary inelastic neutron scattering studies of $W(CO)_3(PCy_3)_2(H_2)$ indicate the presence of M–H_2 modes in the 300–550-cm^{-1} region (Eckert, J.; Swanson, B. I.; Kubas, G. J., unpublished results).
(13) ^1H NMR ($C_6D_5CD_3$, 90 MHz) τ 7.88 (m, J_{HH} = 6.9 Hz), 8.86 (m, J_{HH} = 6.5 Hz), 14.21 (s); $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, 121.5 MHz) δ 33.6 (s, J_{PW} = 273.7 Hz).
(14) Meakin, P.; Gugenberger, L. J.; Peet, W. G.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 1467.
(15) Prepared from 98% HD purchased from MSD Isotopes, Montreal, Canada.
(16) Nageswara Rao, B. D.; Anders, L. R. *Phys. Rev.* **1965**, *140*, A112.

N-Fluoro-*N*-alkylsulfonamides: Useful Reagents for the Fluorination of Carbanions

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While the introduction of fluorine into organic molecules is of broad interest,[1] being used extensively in physical, theoretical, and mechanistic studies and to alter the activity of biomolecules, methodology for the fluorination of carbanions remains limited. Perchloryl fluoride,[2] while an effective reagent for this purpose, is a toxic gas with a tendency to form explosive product mixtures. *N*-fluoroperfluoropiperdine[3] is known to effect anion fluorinations but is very difficult to prepare.[4] Very recently it was shown that treatment of malonate anions with *N*-fluoropyridone[5] affords the corresponding fluorinated derivatives. However, reported yields were low and the scope of the reaction appears to be limited.

We wish to report that *N*-fluoro-*N*-alkylsulfonamides are ef-

Table I. Preparation of *N*-Fluoro-*N*-alkylsulfonamides, RSO_2NFR'

compd[a]	R	R'	F_2, %	yield,[a] %	^{19}F NMR[b]
1	*p*-tolyl	methyl	1	59	−37.62
2	*p*-tolyl	*tert*-butyl	5	14	−62.78
3	*p*-tolyl	*exo*-2-norbornyl	1	47	−46.91
4	*p*-tolyl	*endo*-2-norbornyl	1	71	−36.98
5	*p*-tolyl	cyclohexyl	5	11	−71.63
6	*p*-tolyl	neopentyl	5	57	−36.88
7	*n*-butyl	neopentyl	1	50	−38.40

[a] Products isolated by column chromatography on silica. [b] Upfield from $CFCl_3$.

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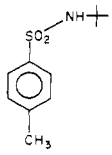
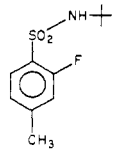
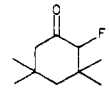
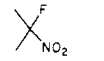
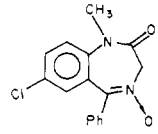
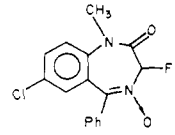
Table II. Fluorination of Anions

example	compd	product[a]	base	solvent	reagent	temp	yield,[a] %	^{19}F NMR[b]
1	$PhCH(COOEt)_2$	$PhCF(COOEt)_2$	NaH	THF	6	RT[f]	81	−162.23
2	$CH_3CH(COOEt)_2$	$CH_3CF(COOEt)_2$	NaH	$PhCH_3$/THF	6	RT	53	−158.02
3	PhMgBr	PhF		Et_2O	2	RT	50[c]	−113.43
4	1-naphthol	2-fluoro-1-naphthol	KH	THF	2	RT	60	−146.78
5			*n*-BuLi	$PhCH_3$/THF	3	RT	55	−112.44
6	anisole	3-fluoroanisole	*n*-BuLi	$PhCH_3$/THF	3	RT	24	−131.22
7			MeLi	$PhCH_3$/THF	3	−20 °C	35	−194.14
8	isobutyrophenone	2-fluoroisobutyrophenone	KH	$PhCH_3$/THF	3	−50 °C	81	−144.52
9	$CH_3(CH_2)_{13}MgBr$	$CH_3(CH_2)_{13}F$		$PhCH_3/Et_2O$	3	−78 °C	15	−218.81
10	indene	1-fluoroindene	KH	$PhCH_3$/THF	3	−50 °C	31	−201.24
11			$(n\text{-Bu})_4NOH$	$PhCH_3$/PhH	2	−20 °C	83[c] 87[d]	−112.38
12	$Ph_2CHCOOH$	$Ph_2CFCOOCH_3$[e]	*n*-BuLi	$PhCH_3$/THF	3	−50 °C	69	−142.33
13			KH	$PhCH_3$/THF	3	−50 °C	52	−177.01

[a] Isolated yield unless otherwise specified. [b] Upfield from $CFCl_3$. [c] Yield by ^{19}F NMR. [d] Yield by GC analysis. [e] Crude product treated with CH_2N_2 before isolation. [f] RT = room temperature.

fective reagents for the selective fluorination of a broad variety of carbanions under mild conditions. The fluorosulfonamides are in general stable compounds, crystalline in many cases, easily prepared[6] by treatment of readily available *N*-alkylsulfonamides with elemental fluorine diluted in nitrogen (eq 1)[7] and isolated

$$RSO_2NHR' \xrightarrow{F_2/N_2} RSO_2NFR' \qquad (1)$$

by standard chromatographic techniques. In a typical reaction, the *N*-alkylsulfonamide is dissolved in a mixture of $CFCl_3/CHCl_3$ (1:1) and the solution cooled to −78 °C. An equivalent amount of fluorine (1–5% in nitrogen) is then bubbled through the solution over 4–6 h. A variety of fluorosulfonamides can be prepared in this way as shown in Table I. The sulfonamides of amines possessing a primary alkyl substituent afford higher yields of the fluorosulfonamide than amines with secondary and tertiary alkyl groups. This results from the competing fluorination of the product fluorosulfonamide (eq 2).[9]

$$RSO_2NFR' \xrightarrow{F_2/N_2} RSO_2F + F_2NR' \qquad (2)$$

Treatment of a carbanion with an *N*-fluoro-*N*-alkylsulfonamide results in transfer of fluorine from nitrogen to carbon (eq 3). A

$$RSO_2NFR' + R''^- \rightarrow R''F + RSO_2NR'^- \qquad (3)$$

broad variety of anions, including malonates, ketone, acid, and amide enolates, and alkyl and aryl organometallics, can be fluorinated in fair to good yield (Table II). The fluorination is specific for carbon anions; the presence of oxygen or nitrogen anions does not affect the reaction (examples 5 and 12). The reaction is favored in nonpolar solvents like benzene, toluene, or hexane over more polar solvents like DMF, THF, or diethyl ether. However, for anion systems that cannot be generated in nonpolar solvents, use of a mixed solvent system is effective. In a typical reaction, the anion is generated in THF or ether, and the solution is diluted with twice the volume of anhydrous toluene and then added dropwise to a solution of the fluorosulfonamide (1–1.5 equiv) in toluene. The reaction temperature is dependent upon the reactivity of the anion. The base and counterion are a matter of convenience although the lithium enolates of ketones and amides are significantly less reactive than their potassium counterparts. For strongly basic anions like alkyl and aryl organometallics, β-elimination of HF from the reagent (R′ = CH_3) can become a major side reaction. Use of a fluorosulfonamide where the tendency toward elimination has been kinetically reduced (R′ = norbornyl or neopentyl) or eliminated (R′ = *tert*-butyl) effectively overcomes this problem. Use of a nonpolar solvent or solvent mixture as described also suppresses elimination.

The application of this methodology to the preparation of agrichemical and pharmaceutical intermediates is presently under investigation, as is the mechanism of the reaction. We feel that the *N*-fluorosulfonamides represent the most broadly useful reagents for the fluorination of organic anions presently available. Use of the reagents does not require any specialized equipment,

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(8) Satisfactory spectral data were obtained for all compounds.

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handling, or safety procedures. The greatest potential may lie in the ability to fluorinate aryl anions. The ability to selectively generate the anions of a broad variety of aromatic compounds has been well established, and other methods for the direct fluorination of aromatics remain limited, especially for electron-deficient systems.

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Registry No. 1, 88303-12-2; **2**, 88303-13-3; **3**, 88303-14-4; **4**, 88303-15-5; **5**, 88303-16-6; **6**, 88303-17-7; **7**, 88303-18-8; $PhCF(COOEt)_2$, 2802-98-4; $CH_3CF(COOEt)_2$, 16519-02-1; PhF, 462-06-6; $CH_3(CH_2)_{13}F$, 593-33-9; $(CH_3)_2CF(NO_2)$, 421-55-6; $Ph_2CFCOOCH_3$, 309-44-4; $PhCH(COOEt)_2$, 83-13-6; $CH_3CH(COOEt)_2$, 609-08-5; PhMgBr, 100-58-3; $CH_3(CH_2)_{13}MgBr$, 88303-25-7; $(CH_3)_2CH(NO_2)$, 79-46-9; $Ph_2CHCOOH$, 117-34-0; 2-fluoro-1-naphthol, 56874-95-4; *N*-(*tert*-butyl)-2-fluoro-4-methylbenzenesulfonamide, 88303-19-9; 3-fluoroanisole, 456-49-5; 2-fluoro-3,3,5,5-tetramethylcyclohexanone, 37783-39-4; 2-fluoroisobutyrophenone, 71057-10-8; 1-fluoroindene, 88303-20-2; 7-chloro-3-fluoro-1-methyl-5-phenyl-1*H*-1,4-benzodiazepin-2-one N^4-oxide, 60628-73-1; *N*-methyl-*p*-toluenesulfonamide, 640-61-9; *N*-(*exo*-2-norbornyl)-*p*-toluenesulfonamide, 88303-21-3; *N*-(*endo*-2-norbornyl)-*p*-toluenesulfonamide, 88303-22-4; *N*-(*tert*-butyl)-*p*-toluenesulfonamide, 2849-81-2; *N*-cyclohexyl-*p*-toluenesulfonamide, 80-30-8; *N*-neopentyl-*p*-toluenesulfonamide, 88303-23-5; *N*-neopentylbutanesulfonamide, 88303-24-6; 1-naphthol, 90-15-3; anisole, 100-66-3; 3,3,5,5-tetramethyl-1-cyclohexen-1-ol acetate, 56763-68-9; isobutyrophenone, 611-70-1; indene, 95-13-6; 7-chloro-1-methyl-5-phenyl-1*H*-1,4-benzodiazepin-2-one N^4-oxide, 2888-64-4.

Photolysis of 3-Chlorodiazirine in the Presence of Alkenes. Kinetic Evidence for Intervention of a Carbene–Alkene Intermediate in Addition of Chlorocarbene to Alkene

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During the course of the studies on the competition between intramolecular 1,2-H shift and intermolecular addition of benzylchlorocarbene to alkene, we obtained chemical evidence for the intervention of a reversibly formed dissociable intermediate in the addition of carbene to alkene, as has been suggested[1] by Turro and Moss in their spectrophotometric studies.

Irradiation of 3-benzyl-3-chlorodiazirines (**1**) in cyclohexane was carried out with a 300-W high-pressure Hg lamp at 10 °C until all of the diazirine was destroyed. A Corning CS-052 filter cutoff at 350 nm was used in order to avoid product isomerization. The photolysis products of **1** were exclusive (*Z*)- and (*E*)-β-chlorostyrenes apparently arising from a 1,2-H shift in the photolytically generated chlorocarbene **2**. When the irradiation of **1** was carried out in the presence of alkenes **4**, 1,2-H migration was appreciably suppressed concomitant with the formation of

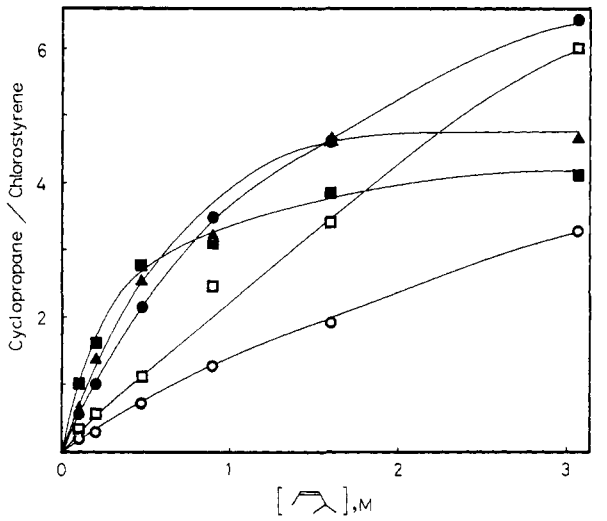
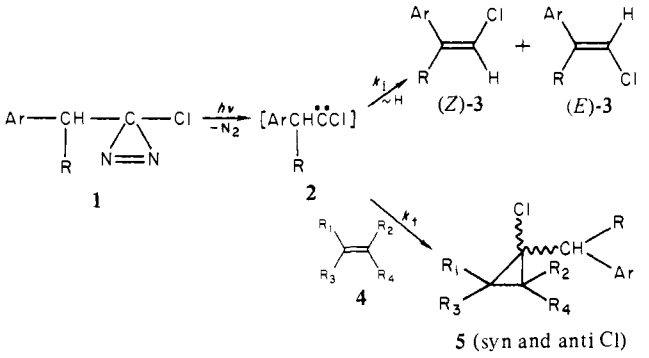


Figure 1. The ratio of intermolecular to intramolecular products as a function of alkene concentration in the reaction of $ArCH_2\ddot{C}Cl$ with (*Z*)-4-methyl-2-pentene: (●) C_6H_5–, (□) 4-MeC_6H_4–, (▲) 4-ClC_6H_4–, (■) 3,4-$Cl_2C_6H_3$–, (○) 4-$MeOC_6H_4$–.

Scheme I



cyclopropanes **5** (see Table I and Scheme I). Addition of the carbene to (*Z*)-4-methyl-2-pentene was stereospecific within the limit of GC detection. This is consistent with the earlier observation[2] that the singlet chlorocarbene is involved in the cyclopropanation.

The intermolecular/intramolecular product ratio (**5**/**3**) varies sensibly with both carbenic and olefinic substitutents, but inspection of the product distributions observed in neat alkene (Table I) did not lead to a relevant structure–reactivity relationship. For example, the product ratio **5**/**3** in the reaction of substituted benzylchlorocarbene **2b–f** with (*Z*)-4-methyl-2-pentene decreased in the order H > 4-Me > 4-Cl > 4-MeO > 3,4-Cl_2, while the order expected from hydride character[2e,3,4] of the 1,2-H migration was 3,4-Cl_2 > 4-Cl > H > 4-Me > 4-MeO. Examination of the product distribution as a function of alkene concentration showed, however, that the order of the product ratio **5**/**3** changed with the alkene concentration. Thus, a plot of the intermolecular/intramolecular product ratio (**5**/**3**) as a function of alkene concentration (e.g., Figure 1) shows pronounced curvature. This cannot be explained in terms of a usual kinetic model for the competitive intermolecular–intramolecular processes for carbene **2** as in Scheme I, which predicts the product ratio **5**/**3** is a linear function of alkene (A) concentration. The results can be better interpreted in terms of a kinetic model recently suggested[1] by

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