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$[HC(py)_3W(NO)_2(CO)](SbF_6)_2$ as a Lewis Acid Precursor in Additions of Silylated *C*-Nucleophiles to Carbonyl Compounds

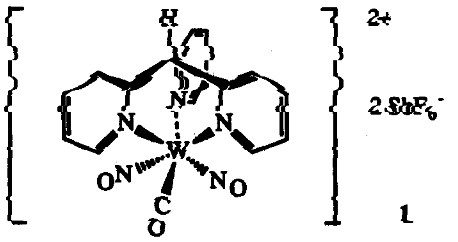
J. W. Faller* and Lise-Lotte Gundersen

Yale University, Department of Chemistry, P. O. Box 6666, New Haven, CT 06511-8118, USA.

Abstract: $[HC(py)_3W(NO)_2(CO)](SbF_6)_2$ is a feasible Lewis acid catalyst precursor for the addition of silylated *C*-nucleophiles to carbonyl compounds. The *O*-silylated adducts are easily isolated without aqueous work-up and the catalyst can be recycled. A remarkable solvent effect is found in the addition of TMS-CN to cyclohexanones.

Lewis acid catalyzed additions of silylated *C*-nucleophiles, such as silyl enol ethers, allylsilanes and silyl cyanides, to carbonyl compounds are important reactions for *C-C* bond formation.[1] Transition metal complex Lewis acids are attractive catalysts for these additions[2] because dramatic effects on the rate and selectivity can be obtained owing to the steric bulk of the ligands as well as to the electronic character of the metal center.

We have recently reported that $[HC(py)_3W(NO)_2(CO)](SbF_6)_2$ **1** (Fig. 1) readily loses the carbonyl ligand giving rise to a 16 electron cation that forms η^1-complexes with aldehydes, ketones and esters.[3] The Lewis acidity of this tungsten species was found to be comparable to that of BF_3 and $AlCl_3$. Complex **1** is easily prepared and can be stored in air for months without significant decomposition. We therefore envisaged that **1** would be a suitable Lewis acid catalyst precursor for the addition of silylated *C*-nucleophiles to carbonyl compounds. The steric bulk of **1** suggested that enhanced stereoselectivity might be found in these reactions.

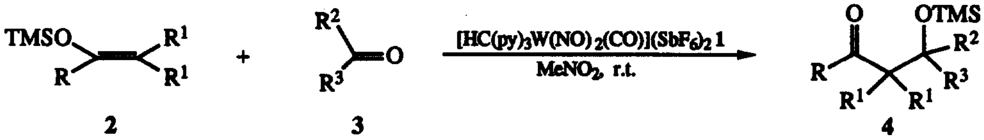


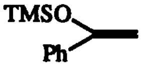
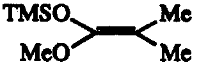
1

Silyl enol ethers **2** added readily to aldehydes in the presence of 5 mol % **1**. The addition to ketones was somewhat slower, but when 10 - 20 mol % **1** was employed, products were obtained in good yields (Table 1).[4] No significant desilylation took place during the reaction, and because aqueous work-up was not required (*vide infra*), the *O*-silylated products **4** could easily be isolated. This might prove to be synthetically useful in certain situations. Even though TMS-ethers are relatively unstable as compared to other trialkylsilyl ethers, the TMS group offers adequate protection for alcohols under a variety of reaction conditions.[5] The very mild work-up conditions also make the catalyst highly suitable for the synthesis of products with other labile substituents.

The tungsten catalyst could be removed from the reaction mixture simply by addition of dichloromethane followed by centrifugation of the resulting suspension.[6] The isolated solid consisted mainly of the active catalyst $[HC(py)_3W(NO)_2](SbF_6)_2$ containing traces of the catalyst precursor **1** as judged by NMR and IR spectroscopy.[7] The recovered tungsten complex also catalyzed the addition of the silyl enol ether **2a** to benzaldehyde; 71% of the product was isolated after a reaction time of 3 h, as compared with 75% when 1 was employed in the same reaction. Passing carbon monoxide through an acetonitrile solution of the recovered material allows it to be transformed back to the catalyst precursor 1. To our knowledge, there is only one previous report of a recyclable Lewis acid catalyst; i.e., ytterbium(III) triflate can be recovered from aldol or Diels - Alder reactions, but only after aqueous work-up.[8]

Table 1. Addition of Silyl Enol Ethers.



Silyl enol ether, 2	R^2COR^3, 3	React. time (h)	mol % 1	Yield (%)4ᵃ
 2a	PhCHO	3.0	5	75
2a	*t*-BuCHO	5.5	5	74
2a	$Ph(CH_2)_2CHO$	3.0	5	77
2a	PhCOMe	4.5	20	73
 2b	PhCHO	2.0	5	88
2b	PhCOMe	4.0	10	76

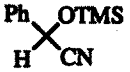
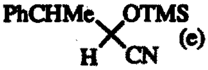
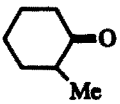
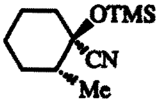
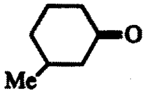
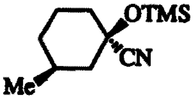
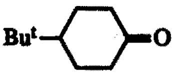
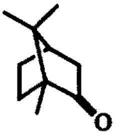
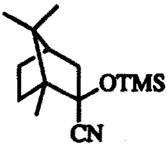
a) Yield of isolated product.

O-silylated cyanohydrins are versatile intermediates in organic synthesis.[9] Addition of trimethylsilyl cyanide 5 to aldehydes and ketones in the presence of a catalytic amount of $[HC(py)_3W(NO)_2(CO)](SbF_6)_2$ 1 gave the adducts 6 in good yields (Table 2).[10] Also in these reactions, the Lewis acid could be recovered as described above. Furthermore, a moderate to high diastereoselectivity was obtained in the additions to some representative cyclohexanones and camphor. The diastereoselectivity obtained in the reactions with the cyclohexanones was, in fact, much higher than what is reported using other Lewis acid catalysts, like zinc iodide or trimethylsilyl triflate.[11] For example, 3-methylcyclohexanone shows only a 2% de with a zinc iodide catalyst under conventional reaction conditions. Presuming that the cyclohexanones are in a chair conformation with the substituent in an equatorial position, the major diastereomeric products are the isomers expected from axial attack on the carbonyl. While large nucleophiles generally attack cyclohexanones from the less hindered equatorial side, small nucleophiles, like the cyanide ion, prefer to attack from the axial side to avoid repulsion between the forming C-R bond and the 2,6-axial bonds.[12] The stereochemical outcome in additions of organometallic reagents to small ring ketones complexed to Lewis acids is sensitive to the size of the complexing agent and these results have been rationalized by a "compression effect".[12] We initially attributed the increased diastereoselectivity using 1 to the greater steric bulk of the tungsten Lewis acid. However, when we conducted the ZnI_2-catalyzed additions in nitromethane, the diastereoselectivity was comparable to what was obtained employing the tungsten catalyst. While this observation could be attributed to a number of factors, the origin of this large solvent effect on zinc iodide catalysis is not fully understood at this time.

In summary, the stable transition metal complex $[HC(py)_3W(NO)_2(CO)](SbF_6)_2$ **1** has been found to be a useful Lewis acid catalyst precursor for the addition of silyl enol ethers and TMS-CN to carbonyl compounds. Comparable diastereoselectivity relative to zinc iodide was generally observed. *O*-silylated adducts are readily isolated because no aqueous work-up is required. This makes the catalyst especially valuable for the synthesis of labile compounds. In contrast to virtually all known Lewis acids, recycling of the catalyst is feasible in most instances.

Table 2. Addition of TMS-CN.

5 3 6

RCOR^1, 3	React. time (h)	Temp. (°C)	Product, 6^a	Yield (%)^b	% de^c	% de ZnI$_2$^{c,d}
PhCHO	1	r.t.		85		
PhCHMeCHO	1	0	 (e)	82	19	21
PhCOMe	10	r.t.		88		
	1 8	0 - 78^f		91 (g)	42 48	47 (32)^h
	1 4	0 - 78^f		91 (g)	76 84	76 (2)^h
	1	0		86	94	83 (80)^h
	23	r.t.		68	43	37

a) The major diastereomer is shown.[13] b) Yield of isolated product. c) Determined with GC. d) Reaction in $MeNO_2$ as described for 1. e) Stereochemistry not determined. f) Reaction in $EtNO_2$. g) Yield of crude product 90 % or better. h) Reaction in CH_2Cl_2, data from ref. 11.

Acknowledgment

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3. Faller, J. W.; Ma, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1579-1586.
4. To a stirring suspension of $[HC(py)_3W(NO)_2(CO)](SbF_6)_2$ **1** (amount, see Table 1) in $MeNO_2$ (2 ml) at ambient temperature under N_2 was added the carbonyl compound **3** (1.0 mmol) and the silyl enol ether **2** (**2a**; 1.1 mmol, **2b**; 1.5 mmol). When TLC showed the reaction to be complete, CH_2Cl_2 (10 ml) was added and the mixture centrifuged.[6] The supernatant was evaporated *in vacuo* and the product purified by flash chromatography on SiO_2 eluting with EtOAc/pentane (1:20).
5. See reference 1, p. 180-184.
6. When the silyl ketene acetal **2b** was used the catalyst could not be recovered. Color change and partial desilylation was observed when **2b** and the tungsten complex **1** was mixed. The same phenomenon has been reported for another transition metal complex.[2b] A possible explanation might be electron transfer from **2b** to the metal complex.
7. ^1H NMR ($MeNO_2$-d_3, 250 MHz); δ 6.67 (s, 1H), 7.6 - 7.8 (m, 3H), 8.1 - 8.4 (m, 6H), 8.7 - 8.9 (m, 3H). IR (MeCN): As reported for $[HC(py)_3W(NO)_2(MeCN)](SbF_6)_2$ and $[HC(py)_3W(NO)_2(CO)](SbF_6)_2$ **1**.[3]
8. Kobayashi, S.; Hachiya, I.; Takahori, T.; Araki, M.; Ishitani, H. *Tetrahedron Lett.* **1992**, *33*, 6815-6818.
9. a) Groutas, W. C.; Felker, D. *Synthesis* **1980**, 861-868. b) Ref. 1, p. 296-299.
10. To a stirring suspension of $[HC(py)_3W(NO)_2(CO)](SbF_6)_2$ **1** (99 mg, 0.1 mmol) in $MeNO_2$ (2 ml) at ambient temperature under N_2 was added the carbonyl compound **3** (1.0 mmol) and the solution cooled to 0 °C before TMS-CN **5** (0.16 ml, 1.2 mmol) was added. When TLC showed the reaction to be complete, CH_2Cl_2 (10 ml) was added and the mixture centrifuged. The supernatant was evaporated *in vacuo* and the product purified by flash chromatography on a short SiO_2 column eluting with EtOAc/pentane (1:5).
11. a) Evans, D. A.; Carroll, G. L.; Truesdale, L. K. *J. Org. Chem.* **1974**, *39*, 914-917. b) Matsubara, S.; Takai, T.; Utimoto, K. *Chem. Lett.*. **1991**, 1447-1450.
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13. The stereochemistry of the major isomer was determined by comparing ^1H NMR and GC with products prepared according to published methods; reaction with *t*-butylcyclohexanone,[11a] 2-methyl- and 3-methylcyclohexanone,[11b] camphor.[14]
14. McIntosh, J. M.; Cassidy, K. C. *Can. J. Chem.* **1991**, *69*, 1315-1319.

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