Reaction of **2** with nickelocene was found to proceed in a 1:2 molar ratio. In a typical preparation, 5.0 mmol of $(C_5H_5)_2Ni$, dissolved in 16 mL of toluene, was added to 5.0 mmol of **2** at −78 °C, and the resulting mixture was stirred for 12 h. $^{31}P\{^1H\}$ NMR spectroscopy revealed the resonances of **1** together with another AX pattern (δ 151.8, 479.1 ppm; J_{PP} = 54.6 Hz) as the only detectable signals. After removal of the solvents and volatiles, the residue was extracted with 15 mL of hexane. The mixture was filtered, and the extracts were evaporated. The solid residue was recrystallized from hexane at −30 °C, yielding **4** as thermally stable and moderately air-sensitive crystals (mp 128–129 °C; yield 38%). The constitution of **4**, which was initially inferred from NMR and mass spectroscopic data,[8] was corroborated by an X-ray structure analysis[9] (Figure 1).

The central tricyclic Ni(1)–Ni(2)–P(1)–P(2)–C(20)–C(19) system of **4** corresponds to a benzvalene analogue, with the double bond between the two carbon atoms. The two phosphorus atoms, P(1) and P(2), which are components of the benzvalene ring, exhibit a μ coordination toward the Ni_2Cp_2 unit. The bonding situation of P(2) corresponds to that found in $\mu(P)$-coordinated phosphinidene complexes,[10] while that of P(1) is equivalent to the situtation in $\mu(P)$-coordinated iminophopshanes.[11] The P–N bond length (155 pm) lies in the range for organo-substituted *trans*-iminophosphanes[12] and corresponds to the value found in the trinuclear cluster obtained by reaction of a tris(iminophosphane)platinum complex with carbon monoxide.[11]

On the basis of the results of metalation reactions of heteroallylic systems containing 2-fold-coordinated phosphorus centers,[3b,7] we proposed an allylic type complex (**3**) as an intermediate. Dimerization upon insertion of the transition metal in the double bond, recycling of **1**, and abstraction of isobutene from the aromatic unit then forms the final product (**4**). Further studies of the reactivity of the allylic anion (**2**) toward reactions with transition-metal complexes are in progress.

Registry No. **1**, 127581-79-7; **2**, 130353-54-7; **4**, 130353-55-8; $(C_5H_5)_2Ni$, 1271-28-9; Mes*PNTms, 86487-13-0; Mes*N=PCl, 124775-15-1.

Supplementary Material Available: Listings of atomic coordinates for non-hydrogen atoms, bond distances and angles, thermal parameters, and hydrogen atom coordinates (7 pages); a listing of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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(8) Spectroscopic and analytical data for compound **4** (MS, EI, 70 eV, m/e (relative intensity); ^1H NMR, δ, C_7D_8; $^{31}P\{^1H\}$ NMR δ, C_7D_8): MS 755 (31, M), 633 (11, M − NiCp), 290 (17.5, Mes*NP); ^1H NMR 1.15 (s, 9 H, *p*-CC*H*-Ar(2)), 1.64 (s, 9 H, *p*-CC*H*-Ar(1)), 1.72 (s, 9 H, *o*-CC*H*-Ar(2)), 1.85 (s, 18 H), *o*-CCH-Ar(1)), 5.79 (s, 10 H, Cp), 7.48 (s, 1 H, arom H, Ar(2)), 7.57 (s, 1 H, arom H, Ar(2)), 7.70 (s, 2 H, arom H, Ar(1)); $^{31}P\{^1H\}$ NMR +151.8, +479.1, $^1J_{PP}$ = 54.6 Hz; yield 35%; mp 128–129 °C. Compound **4** gives a satisfactory analysis.

(9) Some crystal data for **4** are as follows: $C_{42}H_{59}NP_2Ni_2{\cdot}C_7H_8$, M_r = 849.0, monoclinic, space group $P2_1/c$ (No. 14), brownish crystals from toluene, dimensions 0.15 × 0.30 × 0.60 mm^3, a = 1747.7 (9) pm, b = 1200.5 (9) pm, c = 2257.3 (13) pm, β = 104.77 (4)°, V = 4.580 nm^3, Z = 4, D_c = 1.23 g cm^{-3}, μ(Mo Kα) = 0.93 mm^{-1}, 5976 symmetry-independent reflections ($2\theta_{max}$ = 45°), 3868 reflections with $|F| > 4\sigma(F)$ used for the structure solution (direct methods) and refinement (487 parameters), non-hydrogen atoms refined anisotropically, H atoms localized by difference electron density determination and refined with a "riding" model, R = 0.057 (R_w = 0.053, $w^{-1} = \sigma^2(F) + 0.0005F^2$).

(10) Reviews: Huttner, G.; Everts, K. **1986,** *19,* 406. Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987,** *26,* 275.

(11) Scherer, O, J.; Konrad, R.; Guggolz, E.; Ziegler, M. L. *Chem. Ber.* **1983,** *116,* 2676; **1985,** *118, 1.

(12) Niecke, E. Iminophosphines. In *Multiple Bonding and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme Verlag: Stuttgart, FRG, in press. Niecke, E.; Gudat, D. *Angew. Chem., Int. Ed. Engl.*, in press.

A New Approach to *N*-Aryl- and *N*-(2-Heteroaryl)imidates from Chromium Carbenes and Sulfilimines

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Summary: Irradiation of pentacarbonyl(alkoxymethylcarbene)chromium(0) complexes in the presence of a number of *N*-aryl- or *N*-heteroaryl-substituted sulfilimines gives *N*-aryl- or *N*-heteroarylimidates in fair to excellent yields.

Irradiation of chromium carbene (Fischer) complexes is believed to produce ketene–chromium-bonded intermediates in a reversible fashion.[1] Taking advantage of this fact, Hegedus has developed elegant syntheses of β-lactams,[2] α-amino esters,[3] and cyclobutanones.[4] On the other hand, the reactions between these complexes and ylides have been scarcely investigated. Isolation of vinyl ethers in the reaction of pentacarbonyl(methoxyphenylcarbene)tungsten(0) and simple phosphorus ylides has been reported by Casey.[5] 1,1-Diphenylethylene has also been prepared by reacting pentacarbonyl(diphenylcarbene)tungsten(0) and methylenetriphenylphosphorane.[6] Furthermore, sulfoxides react with Fischer carbenes, replacing the metal–carbene bond with a carbon–oxygen double bond.[6,7] No reports referring to the photochemical behavior of chromium carbene complexes toward ylides have appeared to date.

Sulfilimines, having an ylide nature, are known to react with free ketenes, yielding different ketene-derived products.[8] Therefore, either ketene derivatives or imidates

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(1) Hegedus, L. S.; deWeck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988,** *110,* 2122.

(2) Hegedus, L. S.; Imwinkelried, R.; Alarid-Sargent, M.; Dvorak, D.; Satoh, Y. *J. Am. Chem. Soc.* **1990,** *112,* 1109 and references therein.

(3) Hegedus, L. S.; Schwindt, M. A.; DeLombaert, S.; Imwinkelried, R. *J. Am. Chem. Soc.* **1990,** *112,* 2264.

(4) Söderbërg, B.; Hegedus, L. S.; Sierra, M. A. *J. Am. Chem. Soc.* **1990,** *112,* 4364.

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(6) Casey, C. P.; Burkhardt, T.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977,** *99,* 2127.

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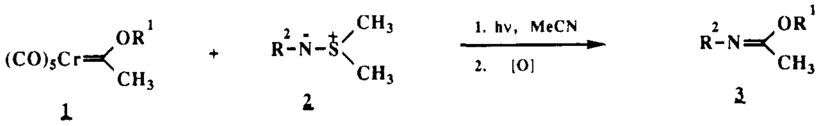
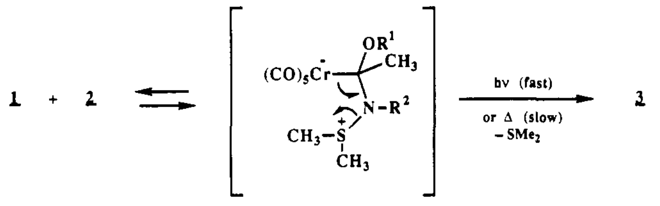
Scheme I



1	2	3	Yield[a]
a: R^1 = Me	a: R^2 = 2-pyridyl	a: R^1 = Me, R^2 = 2-pyridyl	80
b: R^1 = Et	b: R^2 = 2-thiazolyl	b: R^1 = Et, R^2 = 2-thiazolyl	65
	c: R^2 = 2-pyrimidinyl	c: R^1 = Me, R^2 = 2-pyrimidinyl	45
	d: R^2 = p-$NO_2C_6H_4$	d: R^1 = Me, R^2 = p-$NO_2C_6H_4$	52
	e: R^2 = C_6H_5	e: R^1 = Me, R^2 = C_6H_5	70
	f: R^2 = p-$MeOC_6H_4$	f: R^1 = Me, R^2 = p-$MeOC_6H_4$	90

[a] In pure, isolated compound.

Scheme II



4

arising from a Wittig-like reaction analogous to that described by Casey are in principle expected in the photochemical reaction between chromium carbenes and sulfilimines. However, irradiation of chromium carbenes 1 in the presence of sulfilimines 2 yields N-substituted imidates 3 as the sole products (Scheme I).[9] Neither byproducts nor ketene-derived compounds were observed in these reactions. Compounds **3a–f** were obtained as single isomers, even though the possibility of syn–anti isomerism exists. The stereochemistry of these compounds could not be assigned from the physical data available,[10] but it is assumed to be anti on the basis of previous work for this type of compound.[11]

When the reaction between complex **1a** and sulfilimines **2a,e** was carried out at room temperature and in the dark, imidates **3a,e** were also obtained in yields similar to those found under photochemical conditions. However, while less than 2 h is required for completion of the reaction in the presence of light (measured by monitoring the reaction progress by TLC and ^1H NMR spectroscopy, unreacted carbene was detected even after 30 h in the darkness. Although the role of light is not clear to date, if zwitterion 4 in equilibrium with the reagents[12] is assumed to be the reaction intermediate (Scheme II), its otherwise slow, photochemically driven decomposition to give imidates 3 may account for the considerably lower reaction times required under irradiation.

A general experimental procedure for the preparation of compounds 3 is as follows: Chromium alkoxycarbene 1 (1 mmol) was placed in a Pyrex test tube, which was sealed with a rubber septum, evacuated, and purged with argon (three cycles). Degassed MeCN (5 mL) and sulfilimine 2 (1 mmol) in MeCN (5 mL) were added with a syringe. The resulting yellow-orange solution was irradiated for 3 h (450-W Conrad-Hanovia 7825 medium-pressure mercury lamp, Pyrex well) in a water bath. The solvent was removed under reduced pressure, the brown-yellow residue dissolved in EtOAc, and this solution was filtered through Celite, diluted with one volume of hexane, and air-oxidized in an open flask under direct sunlight (usually 10–12 h was required). Filtration of the brown precipitate and solvent removal from the colorless solution gave almost pure imidate.[13] Analytically pure imidates were obtained by flash chromatography.

In summary, the method reported herein represents a new, versatile approach to imidates and is potentially attractive due to mild reaction conditions, good yields, and absence of byproducts. Therefore, it could be an alternative route to those well established for imidate synthesis.[14] For example, *N*-2-heteroaryl-substituted imidates are easily prepared in this way, being unknown or hardly available by "classical" methods.[14] Attempts to extend this reaction to different chromium carbene complexes and other sulfilimines are now in progress.

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Registry No. **1a**, 20540-69-6; **1b**, 25879-46-3; **2a**, 42860-85-5; **2b**, 130408-28-5; **2c**, 54214-58-3; **2d**, 27691-52-7; **2e**, 20094-91-1; **2f**, 27684-98-6; **3a**, 130408-29-6; **3b**, 130408-30-9; **3c**, 130408-31-0; **3d**, 130408-32-1; **3e**, 24433-81-6; **3f**, 24433-83-8.

Supplementary Material Available: Full characterization and spectral data (^1H NMR, ^{13}C NMR, IR, mass spectral, and analytical data) for compounds **3a,f** (4 pages). Ordering information is given on any current masthead page.

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(9) Vinylimidates have been isolated in the reactions of chromium alkoxycarbenes and aziridines. See: Hegedus, L. S.; Kramer, A.; Yijun, C. *Organometallics* **1985**, *4*, 1747. Imidate **3e** has been reported to be formed in the reaction of **1a** or its tungsten analogue and azobenzene. See: (a) Hegedus, L. S.; Lundmark, B. R. *J. Am. Chem. Soc.* **1989**, 111, 9194. (b) Sleiman, H. F.; Mercer, S.; McElwee-White, L. *J. Am. Chem. Soc.* **1989**, *111*, 8007. Imidates have also been reported to be formed in the reaction of $(CO)_5M{=}C(OMe)Ph$ and PhNO. For M = W: Pilato, R. S.; Williams, G. D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 3665. For M = Cr: Herndon, J. W.; McMullen, L. A. *J. Organomet. Chem.* **1989**, *368*, 83.

(10) NOE experiments were carried out for compound **3d**. Upon irradiation of the methyl group at 1.85 ppm a positive NOE enhancement of 1.5% was observed in the ortho aromatic protons (6.85 ppm). Therefore, structural assignments based on these experiments are at best speculative.

(11) (a) Moriarty, R. M.; Yeh, C.-L.; Ramey, K. C.; Whitehurst, P. W. *J. Am. Chem. Soc.* **1970**, *92*, 6360. (b) Yeh, E.-L.; Moriarty, R. M.: Yeh, C.-L.; Ramey, K. C. *Tetrahedron Lett.* **1972**, 2655.

(12) Ylide complexes referred to 4 are known to be in equilibrium with the reagents. See: Kreissl, F. R. In *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, FRG, 1983; pp 156–158, and pertinent references therein.

(13) Compounds 3 are volatile. Considerable loss of material was observed in some cases during the isolation process.

(14) See, for example: Neilson, D. In *The Chemistry of Amidines and Imidates*; Patai, S., Ed.; Wiley-Interscience: New York: 1975; pp 389–412.