Registry No. 1, 109086-56-8; 2, 109086-58-0; 3, 109122-67-0; 4, 109086-61-5; 5, 109086-63-7; 6, 109086-64-8; 7, 109086-66-0; 7·$C_6H_6·H_2O$, 109086-72-8; 8, 109086-68-2; 9, 109086-70-6; 10, 109086-71-7; $HC{\equiv}CCH_2NHCH_3$, 35161-71-8; $HC{\equiv}CH_2NHCH_2C_6H_5$, 1197-51-9; $HC{\equiv}CCH_2N(CH_3)_2$, 7223-38-3; $HC{\equiv}CCH(CH_3)NHCH_3$, 4070-90-0; $HC{\equiv}CCH(n\text{-}C_3H_7)NH_2$, 57964-66-6; $HC{\equiv}CCH(n\text{-}C_3H_7)NHCH_3$, 109086-54-6; $CH_3C{\equiv}CCH_2N(CH_3)_2$, 2588-78-5; $HC{\equiv}CH_2NH_2$, 2450-71-7; $HC{\equiv}CCH(Cl)CH_2CH_2CH_3$, 761-79-5; $HC{\equiv}CCH(NH\text{-}n\text{-}C_4H_9)CH_2CH_2CH_3$, 6281-06-7; $HC{\equiv}CCH(NH\text{-}c\text{-}C_6H_{11})CH_2CH_2CH_3$, 109086-53-5; $HC{\equiv}CCH_2CH_2NH_2$, 14044-63-4; $HC{\equiv}CCH_2NHC_6H_5$, 14465-74-8; $HgCl_2$, 7487-94-7; propargyl bromide, 106-96-7.

Supplementary Material Available: Tables of anisotropic thermal parameters and stereoscopic unit cell diagrams for **6**, **7**, and **10** (6 pages); listings of structure factors for **6**, **7**, and **10** (15 pages). Ordering information is given on any current masthead page.

Formal Nitrogen Hydride Insertion into the Metal–Carbene Bond of Fischer-Type Carbene Complexes

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Received January 29, 1987

A series of imidate complexes $[(CO)_5M\{NH{=}C(OR^1)R^2\}]$ (M = W, R^1 = Me or Et, R^2 = Ph; M = W, R^1 = Me, R^2 = Me; M = Cr, R^1 = Me or Et, R^2 = Ph) can be prepared by reaction of alkoxyorganocarbene complexes with *S*,*S*-diphenylsulfilimine, $NH{=}SPh_2$. The thiocarbene complex $[(CO)_5W\{C(SPh)R^2\}]$ (R^2 = Me) similarly gives the corresponding thioimidate complex, but when R^2 = Ph, $[(CO)_5W(NCPh)]$ (**9**) is the only product. The heterometallocyclic complex $[(CO)_4W\{C(OEt)C(OEt){=}CS(CH_2)_3S\}]$ also undergoes NH insertion and concomitant chelate ring enlargement. The imidate complex $[(CO)_5W\{NH{=}C(OMe)Ph\}]$ (**1**) is deprotonated by Bu^-, H^-, MeO^-, and RS^- to afford the nitrile (**9**), but with dimethylamine the amidine complex $[(CO)_5W\{NH{=}C(NMe_2)Ph\}]$ (**13**) is formed by aminolysis. The *Z* isomer of **1** and the *E* isomer of **13** are completely characterized by X-ray structure determinations. Crystal data for **1**: $WC_{13}H_9NO_6$, M_r 459.07, monoclinic, space group $P2_1/c$, a = 10.694 (4) Å, b = 6.650 (1) Å, c = 20.338 (4) Å, β = 92.18 (3)°, V = 1445 Å^3, Z = 4, D_{calcd} = 2.11 g cm^{-3}. Crystal data for **13**: $WC_{14}H_{12}N_2O_5$, M_r 472.118 monoclinic, space group $P2_1/c$, a = 11.723 (2) Å, b = 9.550 (1) Å, c = 15.032 (6) Å, β = 105.43 (3)°, V = 1622 Å^3, Z = 4, D_{cald} = 1.93 g cm^{-3}. The W–N(sp^2) bond lengths are 2.249 (5) and 2.243 (5) Å. Reaction of $NH{=}SPh_2$ with $[M(CO)_6]$ (M = Cr or W) produces yellow solutions from which $[(CO)_5M(SPh_2)]$ can be isolated. In the presence of PPh_3 only the monosubstituted phosphine complexes form in less than 50% yields.

Introduction

The formal insertion of an NH group into a metal–carbene bond is currently receiving attention; e.g., in E. O. Fischer's group, hydroxylamine has been used for the reaction with terminal carbenes[1] whereas we have employed both of the substituted hydrazines H_2NNMe_2 and H_2NNHMe for carbenes that form part of heterometallocyclic ring systems[2,3] and only the latter for carbene complexes of the type $[(CO)_5M\{C(OEt)CH_2PPh_2\}]$.[3] The main disadvantage of most of these conversions is the unsatisfactory yields due to the formation of various byproducts. Note that the Fischer-type chromium carbene complex $[(CO)_5Cr\{C(OR^1)R^2\}]$ (R^1 = R^2 = Me) gives only the nitrile compound $[(CO)_5Cr(CNR^2)]$ with a substituted hydrazine.[1] The NH group has recently been successfully inserted into metal–carbene bonds containing no heteroatoms,[4] but a similar treatment of alkoxyorganocarbene complexes again affords nitrile complexes.[5]

The present study was undertaken (a) to find a simple quantitative method for introducing an NH unit into the metal–carbene bond of terminal and chelate carbene donor groups and (b) to establish the succeptibility of the formed imidates (from alkoxycarbene complexes) and thioimidates (from thiocarbene complexes) toward reactions such as deprotonation and aminolysis.

Carbene complexes are converted in high yields into enol ethers and phosphine complexes by treatment with the Wittig reagent $CH_2{=}PPh_3$.[6] The isolobal relationships

$$\cdot\dot{\mathrm{N}}\mathrm{H} \underset{\smile}{\longleftrightarrow} \cdot\dot{\mathrm{C}}\mathrm{H}_2$$

$$:\mathrm{SPh}_2 \underset{\smile}{\longleftrightarrow} :\mathrm{PPh}_3$$

that hold between this reagent and the heteroylide diphenylsulfilimine, and the fact that SPh_2 coordinates very weakly to group VI metal carbonyls,[7,8] prompted the use of $NH{=}SPh_2$ for NH insertion. The results reported here are of relevance to the recent preparation of ketimine complexes.[9]

Results and Discussion

Reactions of Alkoxycarbene Complexes with Diphenylsulfilimine. Alkoxyorganocarbene pentacarbonyl

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[1] Fischer, E. O.; Auman, R. *Chem. Ber.* **1968**, *101*, 963.

[2] Lotz, S.; Raubenheimer, H. G.; Viljoen, H. W.; Viljoen, J. C. *S. Afr. J. Chem.* **1983**, *36*, 13.

[3] Raubenheimer, H. G.; Kruger, G. J.; Viljoen, H. W.; Lotz, S. *J. Organomet. Chem.* **1986**, *314*, 281.

[4] Fischer, H.; Zeuner, S. *J. Organomet. Chem.* **1985**, 286, 201.

[5] Fontana, S. Ph.D. Dissertation, Technical University, Munich, 1971.

[6] Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 6543.

[7] Raubenheimer, H. G.; Lotz, S.; Viljoen, H. W.; Chalmers, A. A. *J. Organomet. Chem.* **1978**, *152*, 73.

[8] Herberhold, M.; Süss, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 366.

[9] Czarkie, D.; Shvo, Y. *J. Organomet. Chem.* **1985**, 280, 123.

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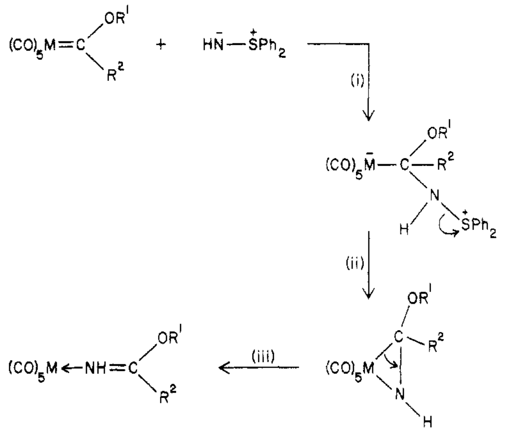
Scheme I



complexes reacted with $HN{=}SPh_2$ in ether at room temperature to produce imidate complexes according to eq 1.

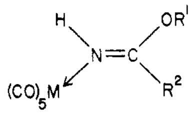
$$(CO)_5M{=}C(OR^1)R^2 + HN{=}SPh_2 \rightarrow (CO)_5M{\leftarrow}NH{=}C(OR^1)R^2 + SPh_2 \quad (1)$$

1–5

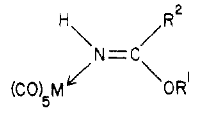
1, M = W, R^1 = Me, R^2 = Ph; **2**, M = W, R^1 = Et, R^2 = Ph; **3**, M = W, R^1 = Me, R^2 = Me; **4**, M = Cr, R^1 = Me, R^2 = Ph; **5**, M = Cr, R^1 = Et, R^2 = Ph

Thin-layer chromatographic and infrared monitoring showed all the conversions to be practically quantitative. The yields given in the Experimental Section correspond to pure products isolated and were not optimized.

All three of the yellow tungsten imidate complexes were present as geometric isomeric mixtures. Relative amounts of isomers present in the crude product mixtures were determined by integration of comparable ^1H NMR resonances, and the *E*/*Z* ratio was 1.2 for **1**, 2.0 for **2**, and 0.7 for **3**. The chromium carbenes underwent insertion stereospecifically under the chosen reactions conditions, and the products consisted of only one isomer each. This result stresses the important role of the group R^2 with regard to the formation of isomers since it has been shown previously that with R^2 = Me an approximately 1:1 isomeric mixture is present at room temperature.[1] A second slow crystallization from ether–hexane gave only one isomer of compound **1**, and an X-ray crystal structure determination confirmed[1] that the metal carbonyl moiety induces a somewhat larger diamagnetic shielding in the group cis thereto than in the trans-situated group. For example (compare Table II) the OMe group of the *Z* isomer resonates at δ 3.81 compared to a 3.82 ppm value for the *E* isomer. When the NMR spectra of compounds **1** and **2** were measured at temperatures between 25 and 60 °C, the relative intensities of comparable resonances in each spectrum remained the same, indicating no isomer interconversion in this temperature range.



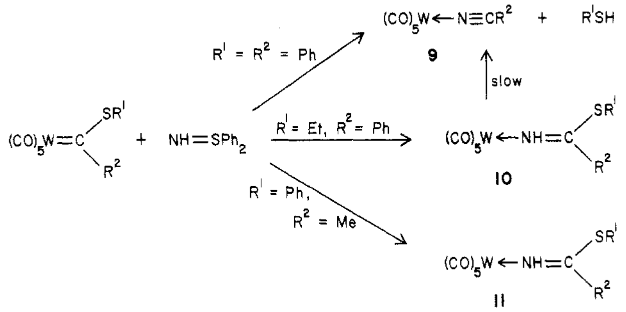
E isomer



Z isomer

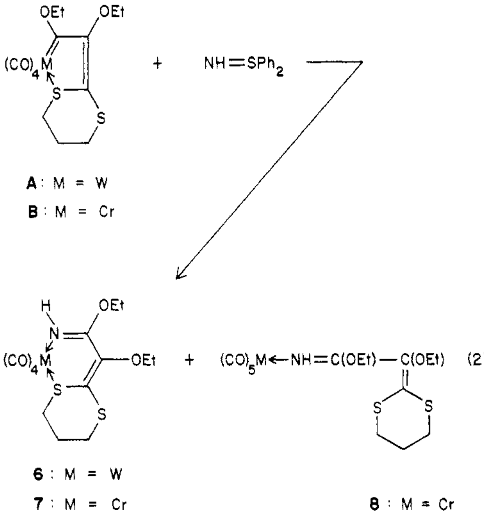
The formal insertion reaction can be explained (Scheme I) in terms of (i) nucleophilic attack by the ylidic nitrogen atom to form an ylide complex,[10] (ii) fragmentation and coordination to form a three-membered chelate (compare the reaction of metal carbonyls with azide ions[11]), and (iii) metal–carbon bond cleavage to give the imidate complex.

Scheme II



The present high yield synthetic method may be extended toward the preparation of free imidates, which are formed from the complexes upon heating to ca. 100 °C.[1] The standard methods of preparation have certain disadvantages.[12]

Reactions of Alkoxycarbene–Thioether Chelates with Diphenylsulfilimine. Previous attempts to effect NH insertion into metal–carbene bonds of alkoxycarbene–thioether chelates produced a number of products from each conversion.[2] Reaction of $[(CO)_4W\{C(OEt)C(OEt){=}CS(CH_2)_3S\}]$ (A) with $NH{=}SPh_2$ now afforded only the tetracarbonyl complex **6** (eq 2) whereas the corresponding chromium chelate B gave mainly (41%) the orange pentacarbonyl imidate complex **8** and less than 5% of the tetracarbonyl compound **7**.



The various factors that lead to either NH insertion (M = W) or NH insertion as well as metal–sulfur bond cleavage and intermolecular CO transfer (M = Cr) are unknown. In previous experiments using Me_2NNH_2 as reactant,[2] A afforded mainly the tungsten pentacarbonyl equivalent of **8** and its chromium counterpart (B), mainly the tetracarbonyl product **7**.

Reactions of Thiocarbene Complexes with Diphenylsulfilimine. The products obtained from the reaction between the thiocarbene complexes $[(CO)_5W\{C(SR^1)R^2\}]$ and $NH{=}SPh_2$ demonstrated the important role played by both organic groups R^1 and R^2 (i) in determining

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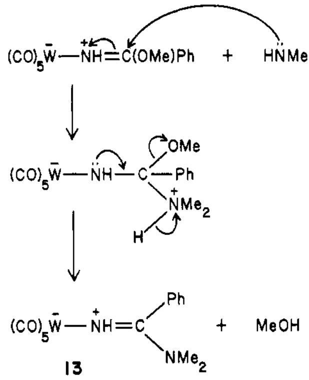
[10] Kreissl, F. R.; Fischer, E. O.; Kreiter, C. G.; Weiss, K. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 563.

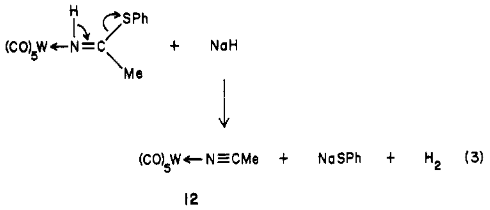
[11] Beck, W.; Werner, H.; Engelman, H.; Smedal, S. *Chem. Ber.* **1968**, *101*, 2143.

[12] Chaturverdi, R. R.; MacMahon, A. E.; Schmir, G. L. *J. Am. Chem. Soc.* **1967**, *89*, 6984.

Scheme III



the stability of the thioimidate complexes toward elimination of HSR^1 (compare Scheme II) as well as (ii) in the geometrical stereoselectivity displayed by the reactions. When R^1 = R^2 = Ph, rapid decomposition of the thioimidate occurred at temperatures as low as -20 °C with the characteristic smell of the thioalcohol evident; only the nitrile complex **9** was isolated. At lower temperatures no insertion took place. With R^1 = Et and R^2 = Ph the insertion product was isolated as an approximately 1:1 mixture of two *E*/*Z* isomers, both of which converted slowly in solution at room temperature into the nitrile complex **9**. Finally, with alkyl and thiophenyl substituents on the carbene carbon atom, insertion gave only one stable isomer (**11**). Deprotonation of **11** at room temperature with sodium hydride in ether immediately generated the acetonitrile complex **12**, in a yield of 90% (eq 3). Free thioimidates spontaneously convert into cyanides and mercaptans.[12]



Reactions of the Imidate Complex $[(CO)_5W\{NH{=}C(OMe)Ph\}]$. (a) Aminolysis. A push-pull type of mechanism, also operative in the aminolysis of Fischer-type carbene complexes, may be used to partly explain the nearly quantitative conversion of the imidate complex (**1**) into a rare example of an amidine complex (**13**). The reaction may be concerted, or an intermediate adduct (shown in Scheme III) may be involved. We used the 1.2:1 isomeric mixture in our experiments. It is difficult to accommodate the occurrence of *E* and *Z* isomers in a ratio of 3:1, which has to be sterically controlled, in this proposal. The *E* isomer was obtained as single crystals by fractional crystallization, and no conversion to the *Z* isomer was observed at room temperature. Its structure was determined by X-ray diffraction. As far as we known, **13** is the first example of a single acyclic metal carbonyl amidine complex. We have previously prepared an amidine that forms part of a chelate ring.[2] Free amidines can be prepared from imidates,[13] and they are thermodynamically more stable than the imidates.[14]

(b) Deprotonation. The spontaneous decomposition of two of the thioimidates (vide supra) led us to attempt a similar conversion with the imidate complex $(CO)_5W\{NH{=}C(OMe)Ph\}$ by deprotonation. The reaction gave the nitrile complex **9** in more than 80% yields when H$^-$, Bu$^-$, or EtO$^-$ were used as bases at room temperature. With EtS$^-$, the reaction was much slower and less than 50% nitrile was finally isolated. No competitive reactions, however, were observed to occur. This type of reaction might also be relevant to the formation of the nitrile $[(CO)_5Cr(N{\equiv}CMe)]$ from $[(CO)_5Cr\{C(OMe)Me\}]$ and MeNHNH$_2$.[4] Finally, no competition between attack of EtO$^-$ at the N-bonded hydrogen and at the sp^2 carbon was observed, since at temperatures lower than -20 °C no reaction occurred.

Table I. Infrared Band Positions (cm^{-1}) for Prepared Complexes

complex	ν(CO)[a]	ν(NH)[b]	ν(CN)[c]
1	2074 (m), 1971 (w), 1932 (vs), 1914 (s)	3350 (m)	1628 (m)
2	2077 (m), 1981 (m), 1929 (vs), 1910 (s)	3341 (m)	1630 (m)
3	2075 (w), 1982 (m), 1929 (vs), 1913 (s)	3336 (m) 3375 (m)	1629 (m)
4	2076 (m), 1988 (w), 1948 (vs), 1932 (s)	3357 (m)	1630 (m)
5	2080 (m), 1980 (w), 1944 (vs), 1929 (s)	3350 (m)	1632 (m)
6	2030 (m), 1929 (m), 1902 (s), 1890 (m)	3358 (m)	
7	2038 (m), 1954 (m), 1905 (s), 1861 (m)	3352 (m)	
8	2076 (m), 1982 (m), 1934 (vs), 1903 (sh)	3410 (m)	
9	2079 (m), 1980 (w), 1942 (vs), 1923 (s)		2243 (w)
10	2071 (m), 1972 (w), 1933 (vs), 1915 (s)	3289 (s) 3237 (m)	1631 (m)
11	2074 (w), 1981 (w), 1930 (vs), 1916 (s)	3307 (m)	1631 (m)
12	2078 (m), 1980 (w), 1940 (vs), 1924 (s)		2245 (w)
13	2070 (w), 1964 (w), 1924 (vs), 1887 (sh)	3339 (w) 3431 (w)	1602 (m)

[a] Measured in hexane. [b] Measured in Nujol (4, 5, and 13) or in hexachlorobutadiene (the rest). [c] Measured in hexachlorobutadiene (1–3, 10) or in Nujol (11) as oils (4, 5, and 13) or as KBr pellets (9 and 12).

Spectral Characterization of Isolated Compounds. The infrared spectra of the new imidates and amidines in the carbonyl region display the typical A$_1^{(1)}$, B$_1$, E, and A$_1^{(2)}$ pattern of pentacarbonylmetal complexes with pseudo C_{4v} symmetry (Table I). The ν(CO) frequencies of compounds **6**, **7**, and **8** correspond well with previously reported values in the same solvent.[2] From the values of the A$_1^{(2)}$ vibration mode of the tungsten complexes which reflect the stretching frequency of the CO group trans to the nitrogen-donor ligand, it follows that the σ(donor)/π(acceptor) ratio of the imine and nitrile ligands increases in the series $N{\equiv}CR$ (R = Me or Ph) < $NH{=}C(SR^1)R^2$ (R^1 = Et or Ph when R^2 = Ph or Me) ≤ $NH{=}C(OR^1)R^2$ (R^1 = Me or Et; R^2 = Ph or Me) ≪ $NH{=}C(NMe_2)Ph$. The ν(C=N) frequency of the amidine compound at 1602 cm^{-1} is much lower than that of the imidate complexes which characteristically appears at 1630 ± 2 cm^{-1}. The weak to medium-strong NH frequencies vary between 3237 and 3410 cm^{-1}. Each of the compounds **3**, **10**, and **13** exhibits two bands compared to one band for the other compounds.

With regard to other types of ligands, the following σ(donor)/π(acceptor) series (once again based on the A$_1^{(2)}$ frequencies) indicate that more negative charge is effectively transferred on to the metal by the imidate and amidine ligands than by most other monodentate ligands

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(13) Sandler, S. R.; Karo, W. *Organic Functional Group Preparation*; Academic: New York, 1972; Vol. 3, Chapter 8.

(14) Hafelinger, G. *Tetrahedron* 1971, *27*, 1635.

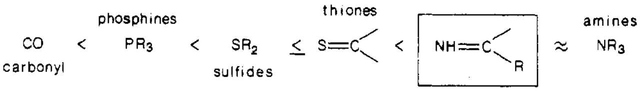
Table II. ^{1}H NMR Spectra of the Complexes

complex (isomer)	δ ($CDCl_3$, relative to Me_4Si)
1 (*Z*)	7.45 (m, 5 H, Ph), 6.82 (br, 1 H, NH), 3.81 (s, 3 H, OMe)
1 (*E*)	7.29 (m, 5 H, Ph), 6.82 (br, 1 H, NH), 3.82 (s, 3 H, OMe)
2 (*Z*)	9.28 (br, 1 H, NH), 7.40 (m, 5 H, Ph), 4.12 (q, 2 H, OCH_2Me), 1.40 (t, 3 H, Me)
2 (*E*)	9.28 (br, 1 H, NH), 7.36 (m, 5 H, Ph), 4.14 (q, 2 H, OCH_2Me), 1.44 (t, 3 H, M)
3 (*Z*)	6.77 (br, 1 H, NH), 3.73 (s, 3 H, OMe), 2.30 (s, 3 H, Me)
3 (*E*)	6.77 (br, 1 H, NH), 3.96 (2 3 H, OMe), 2.23 (s, 3 H, Me)
4	6.59 (br, 1 H, NH), 7.32 (m, 5 H, Ph), 3.81 (s, 3 H, OMe)
5	7.51 (m, 5 H, Ph), 6.54 (br, 1 H, NH), 4.03 (q, 2 H, OCH_2Me), 1.40 (t, 3 H, Me)
10 (*Z*)	8.83 (br, 1 H, NH), 7.51 (m, 5 H, Ph), 2.65 (q, 2 H, SCH_2Me), 1.16 (t, 3 H, Me)
10 (*E*)	7.74 (br, 1 H, NH), 7.35 (m, 5 H, Ph), 2.90 (q, 2 H, SCH_2Me), 1.38 (t, 3 H, Me)
11 (*Z*)	8.20 (br, 1 H, NH), 7.58 (m, 5 H, Ph), 2.41 (s, 3 H, Me)
11 (*E*)	8.20 (br, 1 H, NH), 7.64 (m, 5 H, Ph), 2.42 (s, 3 H, Me)
13 (*Z*)	7.44 (m, 5 H, Ph), 5.85 (br, 1 H, NH), 2.880 and 2.886 (s, 6 H, NMe_2)
13 (*E*)	7.38 (m, 5 H, Ph), 5.85 (br, 1 H, NH), 2.922 and 2.928 (s, 6 H, NMe_2)

Table III. Selected ^{13}C NMR Data (Room Temperature)

complex (isomer)	δ ($CDCl_3$, relative to Me_4Si)
1 (*Z*)	201.1 (trans CO), 198.3 (cis CO), 177.2 (NC), 127-136 (Ph), 57.5 (OMe)
1 (*E*)	201.9, 197.9, 179.3, 127-136, 60.1
2 (*Z*)	201.3 (trans CO), 198.4 (cis CO), 176.1 1 (NC), 127-136 (Ph), 64.6 (OCH_2), 14.5 (Me)
2 (*E*)	202.0, 198.0, 177.9, 127-136, 69.5, 15.5
3 (*Z*)	201.3 (trans CO), 198.8 (cis CO), 175.1 (NC), 127-136 (Ph), 61.2 (OMe), 14.8 (Me)
3 (*E*)	202.0, 198.0, 176.9, 127-136, 63.7, 15.8
4	221.7 (trans CO), 216.0 (cis CO), 180.1 (NC), 127-136 (Ph), 60.3 (OMe)
5	221.0 (trans CO), 215.5 (cis CO), 178.9 (NC), 127-136 (Ph), 68.9 (CH_2), 15.4 (Me)

which afford stable pentacarbonyltungsten or -chromium complexes:[7,15,16]



The ^{1}H NMR resonances of all the new complexes are given in Table II. Due to restricted rotation around the HNC–N bond at room temperature, two resonances were assigned to the methyl groups in each of the isomers of **13**. The chemical shifts for compounds **6–8** corresponded to published values.[2] For the latter compound as well as for the other two new chromium compounds the presence of only one isomer was detected. The organic group attached to the carbene carbon is important in this respect since a similar insertion (by using NH_2OH) in the carbene complex $[(CO)_5Cr\{C(OMe)Me\}]$ effects both *E* and *Z* isomers in an approximate ratio of 1:1 at room temperature (and in equilibrium with each other).[1]

^{13}C NMR spectral data for compounds **1–5** are collected in Table III. For the tungsten compounds the resonances for the N-bonded sp^2 carbon atoms in the *E* isomers are characteristically somewhat higher (δ 177–179) than for the *Z* isomes (δ 175–177). Values for chromium complexes are slightly higher than for their tungsten counterparts.

Mass spectra of the new complexes gave *m/z* values corresponding to the molecular ions which then consecutively lost five carbonyl groups.

Crystal Structures of $[(CO)_5W\{NH{=}C(OMe)Ph\}]$ (1) and $[(CO)_5W\{NH{=}C(NMe_2)Ph\}]$ (13). The structures of these two monomeric pentacarbonyltungsten complexes containing N-donor ligands are shown in Figures 1 and 2. Bond lengths and angles are given in Table IV.

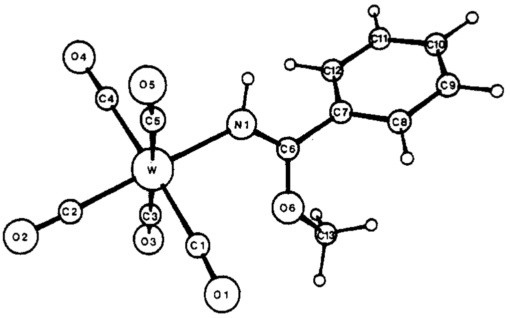


Figure 1. Structure of $[(CO)_5W\{NH{=}C(OMe)Ph\}]$ (1).

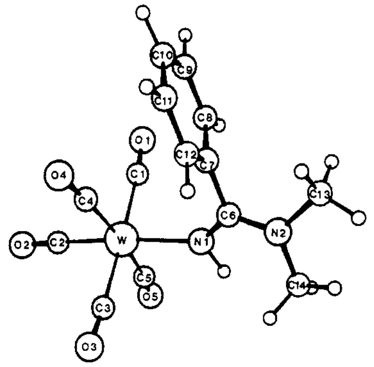


Figure 2. Structure of $[(CO)_5W\{NH{=}C(NMe_2)Ph\}]$ (13).

Apart from the fact that **1** is the *Z* isomer and **13** the E isomer, the general bonding characteristics of the two complexes along the $(CO)_5W$–NH–C–Ph backbone are essentially similar. The W–N distances are the same (average 2.246 Å), and very small differences occur in the W–CO(trans) bond lengths (1.981 (7) Å in the imidate and 1.954 (7) Å in the amidine) and in the W–N–C(6) angles (129.6 (5)° in **1** vs. 135.9 (5)° in **13**) whereas the N–C(6) distances differ by 0.028 Å (1.276 (8) Å for **1** against 1.303 (7) Å for **13**). The W–N distances in the new octahedral complexes are markedly longer than the average W–N separation of 2.207 Å previously found in the bridged carbonyl complex $[(CO)_5W]_2(N_2C_2Me_4)$.[17] The N(2)–C(6) bond of 1.349 (7) Å in **13** is shorter than the single bonds N(2)–C(13) and N(2)–C(14) (average 1.455 Å), consistent with the restricted rotation observed in the ^{1}H NMR spectrum, but is still significantly longer than the N(1)–C(6) double bond (1.303 (7) Å). C(14) is almost coplanar with N(1), C(6), C(9), and N(2), but C(13) is not, as indicated by the torsional angles in **13**: N(1)–C(6)–N(2)–C-

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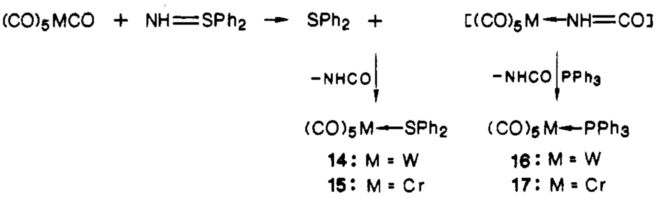
Table IV. Bond Lengths (Å) and Angles (deg) for $[(CO)_5W\{NH{=}C(OMe)Ph\}]$ (1) and $[(CO)_5W\{NH{=}C(NMe_2)Ph\}]$ (13)

compd	1	13
	Bond Lengths	
W–N(1)	2.249 (5)	2.243 (5)
W–C(1)	1.998 (8)	2.054 (8)
W–C(2)	1.981 (7)	1.954 (7)
W–C(3)	2.020 (8)	2.034 (8)
W–C(4)	1.992 (8)	2.010 (7)
W–C(5)	2.002 (8)	2.039 (7)
O(1)–C(1)	1.171 (7)	1.123 (8)
O(2)–C(2)	1.142 (7)	1.155 (7)
O(3)–C(3)	1.150 (8)	1.129 (8)
O(4)–C(4)	1.178 (8)	1.153 (7)
O(5)–C(5)	1.168 (8)	1.141 (7)
O(6)–C(6)	1.309 (8)	
O(6)–C(13)	1.427 (7)	
N(1)–C(6)	1.276 (8)	1.303 (7)
N(2)–C(6)		1.349 (7)
N(2)–C(13)		1.464 (7)
N(2)–C(14)		1.446 (7)
C(6)–C(7)	1.496 (8)	1.486 (8)
C(7)–C(8)	1.391 (9)	1.392 (9)
C(7)–C(12)	1.371 (8)	1.403 (8)
C(8)–C(9)	1.395 (9)	1.338 (10)
C(9)–C(10)	1.376 (9)	1.366 (13)
C(10)–C(11)	1.371 (9)	1.377 (13)
C(11)–C(12)	1.400 (9)	1.394 (11)
	Bond Angles	
N(1)–W–C(1)	92.4 (2)	91.6 (2)
N(1)–W–C(2)	179.8 (1)	175.7 (2)
C(1)–W–C(2)	87.5 (3)	91.1 (3)
N(1)–W–C(3)	91.8 (2)	89.6 (2)
C(1)–W–C(3)	90.7 (3)	178.8 (3)
C(2)–W–C(3)	88.4 (3)	87.8 (3)
N(1)–W–C(4)	90.3 (2)	95.9 (2)
C(1)–W–C(4)	175.5 (3)	91.5 (3)
C(2)–W–C(4)	89.8 (3)	87.4 (3)
C(3)–W–C(4)	92.8 (3)	88.0 (3)
N(1)–W–C(5)	90.1 (2)	92.6 (2)
C(1)–W–C(5)	88.7 (3)	89.7 (3)
C(2)–W–C(5)	89.7 (3)	84.1 (3)
C(3)–W–C(5)	178.0 (3)	90.7 (3)
C(4)–W–C(5)	87.8 (3)	171.4 (3)
C(6)–O(6)–C(13)	122.4 (5)	
W–N(1)–C(6)	129.6 (5)	135.9 (5)
W–C(1)–O(1)	175.6 (6)	175.1 (8)
W–C(2)–O(2)	179.5 (6)	178.7 (6)
W–C(3)–O(3)	177.9 (7)	175.9 (7)
W–C(4)–O(4)	174.5 (7)	173.3 (6)
W–C(5)–O(5)	174.8 (6)	171.7 (6)
O(6)–C(6)–N(1)	118.3 (6)	
O(6)–C(6)–C(7)	120.1 (6)	
C(6)–N(2)–C(13)		123.1 (6)
C(6)–N(2)–C(14)		119.5 (5)
C(13)–N(2)–C(14)		115.9 (6)
N(1)–C(6)–N(2)		123.8 (6)
N(2)–C(6)–C(7)		117.4 (6)
N(1)–C(6)–C(7)	121.5 (6)	118.9 (6)
C(6)–C(7)–C(8)	119.0 (6)	119.7 (7)
C(6)–C(7)–C(12)	119.7 (6)	118.7 (7)
C(8)–C(7)–C(12)	121.2 (6)	121.5 (7)
C(7)–C(8)–C(9)	119.0 (7)	118.5 (8)
C(8)–C(9)–C(10)	120.4 (7)	120.6 (11)
C(9)–C(10)–C(11)	119.6 (7)	121.0 (12)
C(10)–C(11)–C(12)	121.3 (7)	120.5 (11)
C(7)–C(12)–C(11)	118.4 (7)	117.8 (9)

(14) = 4 (1)° and N(1)–C(6)–N(2)–C(13) = 162 (1)°. The already mentioned W–N(1)–C(6) angle of 136° in **13** reveals a significant portion of s character in the bond between the nitrogen atom and the metal.

Reaction of *S*,*S*-Diphenylsulfilimine with $[(CO)_6M]$ (M = Cr or W). The similarity in bonding characteristics of carbene, isocyanide, and carbonyl ligands has been stressed previously[18,19] and now prompted a preliminary investigation of NH insertion into the metal–carbonyl bond. A nucleophilic attack on a carbonyl carbon atom of group VI metal carbonyls leading to anionic complexes of the type $[(CO)_5M(NCO)]^-$ has been referred to above.[11]

Scheme IV



Treatment of $[(CO)_6M]$ (M = Cr or W) solutions in tetrahydrofuran with $NH{=}SPh_2$ rapidly produced a color change to sharp yellow, and the known complexes $[(CO)_5M(SPh_2)]$[7,8] were isolated by column chromatography. In the presence of excess triphenylphosphine the same procedure gave $[(CO)_5M(PPh_3)]$[20] in moderate yields. A carbonyl group was not substituted by PPh_3 in the absence of $NH{=}SPh_2$, and it is known that the sulfide coordinates much weaker than the phosphine.[2] We propose that the reactions involved the intermediate shown in Scheme IV.

The formed products were characterized by comparison of their infrared and mass spectral data with published results. The weakly bonded NH-inserted complexes could not be isolated, but a mass spectrum of the crude reaction mixture of the $[(CO)_6W]$ reaction after it had been stripped of solvent contained peaks at *m*/*z* values of 367 and 43 corresponding to the molecular masses of the isocyanic acid complex and isocyanic acid, respectively. In addition, an infrared spectrum of this residue showed a strong absorption band at 2247 cm^{-1} indicating the N=C=O fragment.[11] We established that compound **17** also formed quantitatively by substitution of PPh_3 for SPh_2 and such a substitution can also not be ruled out completely during the formation of **16** and **17**. Nitrogen hydride insertion into a variety of metal–carbonyl and metal–isocyanide bonds is presently under further investigation.

Experimental Section

Materials and Methods. All reactions and manipulations were performed under nitrogen in Schlenk apparatus. Solvents were dried by conventional methods and distilled under nitrogen. *S*,*S*-Diphenylsulfilimine (Aldrich) was degassed under high vacuum and saturated with nitrogen before use. The carbene complexes used as starting materials were prepared according to literature procedures.[21] Infrared spectra were determined by using a Perkin-Elmer 297 instrument. NMR spectra were recorded on a Varian VXR 200 spectrometer. For mass measurements a Finnigan Mat Model 8200 was used. Melting points (uncorrected) were determined on a Kofler hot-stage apparatus. Elemental analyses were carried out by the analytical laboratory of the South African CSIR in Pretoria. The numbers of the compounds refer to the drawings in the Results and Discussion.

Reactions of Carbene Complexes with *S*,*S*-Diphenylsulfilimine. Synthesis of $[W(CO)_5\{NH{=}C(OMe)Ph\}]$ (1). A solution of $[W(CO)_5\{C(OMe)Ph\}]$ (397 mg, 0.89 mmol) in 25 mL of diethyl ether was treated with 180 mg (0.89 mmol) of *S*,*S*-diphenylsulfilimine. The red solution turned yellow immediately

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Table V. Crystallographic Data for [(CO)$_5$W{NH=C(OMe)Ph}] (1) and [(CO)$_5$W{NH=C(NMe$_2$)Ph}] (13) and Structure Determination Details

	1	13
	Crystal Data	
formula	$WC_{13}H_9NO_6$	$WC_{14}H_{12}N_2O_5$
cryst habit	yellow plates	yellow prisms
cryst size, mm	0.35 × 0.20 × 0.15	0.20 × 0.20 × 0.20
symmetry	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
unit-cell determination: least-squares fit to	25 reflections, θ(Mo) < 10°	25 reflections, θ(Mo) < 18°
unit-cell dimensions (Å)	a = 10.694 (4)	a = 11.723 (2)
	b = 6.650 (1)	b = 9.550 (1)
	c = 20.338 (4)	c = 15.032 (6)
	β = 92.18 (3)°	β = 105.43 (3)°
packing: V(Å^3), Z	1445, 4	1622, 4
D_{calcd} (g cm^{-3}), M, F(000)	2.11, 459.07, 864	1.93, 472.11, 896
	Experimental Data	
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiatn	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
monochromator	graphite	graphite
collectn mode	ω–2θ, scans, θ range 3–27°	ω/2θ scans, θ range 3–25°
scan width	(0.5 + 0.4 tan θ)°	(0.5 + 0.4 tan θ)°
scan speed	variable, 5.5° min^{-1}	variable, 5.5° min^{-1}
reflctns measd	3419	3030
observable reflctns	2765 with $F > 3\sigma$	2292 with $F > 2\sigma$
stability	3 reflections every 60 min, no variation	3 reflections every 60 min, 2% loss in intensity
correctns	Lp; absorption; anomalous dispersion	Lp; crystal decay; absorption; anomalous dispersion
μ, cm^{-1}	76.7	68.3
absorptn correctns	empirical[24]	empirical[24]
	Solution and Refinement	
soln	SHELX76[25]	SHELX76[25]
refinement	least squares, full matrix	least squares, full matrix
no. of variables	195	206
reflctns used	1765 observed with $F > 3\sigma$	2292 observed with $F > 2\sigma$
weighting scheme	$w = (\sigma(F))^{-2}$	$w = (\sigma(F))^{-2}$
final Δ peaks	1.3 e Å^{-3} near the W atom	0.9 e Å^{-3} near the W atom
final R, R_w	0.036, 0.027	0.032, 0.021
scattering factors	ref 26	ref 26

and was filtered through silica gel after stirring for 15 min. The solvent was removed in vacuo. NMR data (^{1}H and ^{13}C) of the crude mixture indicated the presence of both *E* and *Z* isomers. Recrystallization from diethyl ether and large excess of hexane afforded 250 mg (61%) of **1**. Anal. Calcd. for $C_{13}H_9NO_5W$: C, 34.00; H, 1.97; N, 3.05. Found: C, 34.09; H, 1.85; N, 3.10. Slow crystallization (–30 °C) from a 2:1 mixture of ether and hexane gave only the *Z* isomer, decomp at 91–94 °C.

Synthesis of Compounds 2–5. Products **2** and **3** were prepared from [W(CO)$_5${C(OEt)Ph}] and [W(CO)$_5${C(OMe)Me}] according to a similar procedure as above in yields of 57.4 and 78.5%, respectively. The powdery mixtures containing *E* and *Z* isomers, obtained by precipitation from diethyl ether and a large excess of hexane, both analyzed correctly, and **3** decomposed between 71 and 72 °C. It was possible to separate the isomers of **2** by fractional crystallization from diethyl ether–hexane (1:2) and the *Z* isomer decomposed at a higher temperature (75–78 °C) than its *E* counterpart (70–73 °C). Anal. Calcd for $C_{14}H_{11}NO_6W$ (**2**): C, 35.60; H, 3.27; N, 2.95. Found: C, 35.53; H, 2.34; N, 2.98. Calcd for $C_8H_7NO_6W$ (**3**): C, 24.20; H, 1.77; N, 3.53. Found: C, 24.06; H, 1.68; N, 3.56.

The chromium-containing products **4** and **5** were less stable and the yields obtained also lower (ca. 56 and 28% respectively). These oily compounds were not analyzed but characterized spectroscopically.

Synthesis of Compounds 6–8. [(CO)$_4$W{C(OEt)C(OEt)=CS(CH$_2$)$_3$S}] (300 mg, 0.57 mmol) was dissolved in 20 mL of dichloromethane. The solution was cooled to –10 °C, *S*,*S*-diphenylsulfilimine (114 mg, 0.57 mmol) added, and the mixture stirred for 45 min at this temperature. The color changed from violet to orange-red. The solution was filtered through silica gel and the volume then reduced to 10 mL reduced pressure. Addition of 10 mL of hexane and cooling to –20 °C produced orange crystals (176 mg, 57%) of **6**. Its melting point as well as its ^{1}H NMR and infrared spectra corresponded to those of an authentic sample.[2] With the chromium analogue (200 mg, 0.50 mmol) as starting material, thin-layer chromatography indicated the formation of two products. The mixture was transferred to a cooled (–10 °C) SiO$_2$ column and eluted with diethyl ether–hexane (1:2). Two fractions were collected. The red fraction contained less than 5% of the chelate **7**, and the major product (**8**, 90 mg) was obtained from the yellow fraction in 40.6% yield after stripping of solvent in vacuo. Compounds **7** and **8** were characterized by comparison of their ^{1}H NMR and infrared spectra with literature data.[2]

Deprotonation of Imidate and Thioimidate Complexes. A solution of [(CO)$_5$W{NH=C(OMe)Ph}] (150 mg, 0.33 mmol) in diethyl ether was treated at –20 °C with LiBu (0.60 mL, 0.65 M, 0.39 mmol). After being stirred for 30 min, the yellow mixture was filtered through silica gel and the solvent evaporated under vacuum. Yellow [(CO)$_5$W(N≡CPh)][22] (**9**) (113 mg, 80%) was the only product obtained. With equimolar amounts of the bases NaH and NaOEt the result was the same, but with NaSEt the reaction was much slower, and even at room temperature after the same period of time, less than 50% conversion occurred. Deprotonation of [(CO)$_5$W{NH=C(SPh)Me}] (**11**) (vide infra) (300 mg, 0.63 mmol) with NaH at room temperature gave [(CO)$_5$W{N≡CMe}][23] (**12**) (198 mg, 86.2%) after filtration through SiO$_2$, removal of the solvent in vacuo, and recrystallization from diethyl ether–hexane (1:2). Compounds **9** and **12** gave the correct molecular ions in their mass spectra and infrared spectra and melting points also corresponded with literature values.

Reactions of Thiocarbene Complexes with *S*,*S*-Diphenylsulfilimine. Reaction of [(CO)$_5$W{C(SEt)Ph}] (360 mg, 0.78 mmol) in 30 mL of diethyl ether with NH=SPh$_2$ (156 mg,

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Table VI. Fractional Coordinates (×10⁴; ×10⁵ for W) and Equivalent[a] Isotropic Temperature Factors (Å² × 10³; ×10⁴ for W) for the Non-Hydrogen Atoms for $[(CO)_5W\{NH{=}C(OMe)SPh\}]$ (1) and $[(CO)_5W\{NH{=}C(NMe_2)Ph\}]$ (13)

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)
		Compound 1		
W	12608 (2)	13907 (5)	88050 (1)	372 (2)
O(1)	707 (5)	3063 (9)	10222 (2)	70 (4)
O(2)	3958 (4)	3105 (9)	9047 (2)	70 (4)
O(3)	500 (5)	5594 (9)	8173 (3)	74 (4)
O(4)	2143 (5)	−532 (10)	7476 (3)	82 (4)
O(5)	2205 (5)	−2703 (8)	9446 (3)	64 (3)
O(6)	−1748 (4)	2713 (8)	9020 (2)	48 (3)
N(1)	−678 (5)	142 (9)	8631 (3)	38 (3)
C(1)	860 (6)	2428 (11)	9694 (4)	43 (4)
C(2)	2970 (6)	2484 (12)	8961 (4)	51 (4)
C(3)	763 (6)	4050 (13)	8393 (3)	47 (4)
C(4)	1775 (6)	248 (12)	7951 (4)	52 (4)
C(5)	1805 (6)	−1199 (13)	9228 (3)	41 (4)
C(6)	−1735 (6)	929 (11)	8749 (3)	38 (4)
C(7)	−2933 (5)	−192 (10)	8622 (3)	36 (4)
C(8)	−3648 (6)	−723 (11)	9152 (4)	49 (4)
C(9)	−4746 (6)	−1821 (12)	9036 (4)	57 (5)
C(10)	−5123 (7)	−2347 (12)	8405 (5)	56 (5)
C(11)	−4407 (7)	−1799 (13)	7889 (4)	61 (5)
C(12)	−3284 (6)	−740 (11)	7992 (3)	51 (4)
C(13)	−2847 (6)	3931 (11)	9018 (3)	48 (4)
		Compound 13		
W	14408 (3)	28327 (3)	75769 (2)	369 (2)
O(1)	1172 (6)	218 (6)	6233 (5)	89 (5)
O(2)	861 (4)	916 (5)	9070 (4)	58 (3)
O(3)	1758 (5)	5274 (6)	9043 (4)	80 (4)
O(4)	4110 (5)	2064 (7)	8519 (4)	87 (5)
O(5)	−1351 (4)	3173 (6)	7033 (4)	70 (4)
N(1)	1741 (5)	4333 (5)	6514 (4)	43 (3)
N(2)	2664 (5)	5765 (6)	5650 (4)	46 (3)
C(1)	1262 (7)	1181 (9)	6675 (6)	60 (6)
C(2)	1090 (6)	1621 (7)	8518 (5)	42 (4)
C(3)	1626 (6)	4439 (8)	8494 (5)	51 (4)
C(4)	3158 (6)	2385 (8)	8132 (5)	56 (5)
C(5)	−346 (6)	3127 (7)	7177 (5)	48 (4)
C(6)	2597 (6)	4592 (7)	6134 (4)	39 (4)
C(7)	3562 (6)	3547 (8)	6234 (5)	41 (4)
C(8)	3331 (7)	2272 (8)	5772 (5)	58 (5)
C(9)	4248 (10)	1314 (10)	5879 (7)	82 (8)
C(10)	5348 (11)	1612 (13)	6433 (9)	88 (10)
C(11)	5588 (9)	2891 (14)	6867 (7)	82 (8)
C(12)	4694 (6)	3882 (9)	6788 (5)	61 (5)
C(13)	3410 (6)	5881 (8)	5012 (5)	53 (5)
C(14)	1785 (7)	6851 (7)	5581 (5)	62 (5)

[a] U_{eq} is defined as the geometric mean of the diagonal elements of the diagonalized matrix $\mathbf{U}_{ij}$.

0.96 mmol) at room temperature produced after 5 min two yellow products which were separated by column chromatography (SiO_2, −10 °C; eluant diethyl ether–hexane, 1:1). The first product eluted was $[(CO)_5W(N{\equiv}CPh)]$ (**9**) in ca. 10% yield. The compound $[(CO)_5W\{NH{=}C(SEt)Ph\}]$ (**10**) was obtained (226 mg, 62.7%) from the second yellow fraction after removal of solvent under reduced pressure at 0°C. Anal. Calcd. for $C_{14}H_{11}NO_5SW$: C, 34.38; H, 2.27; N, 2.86. Found: C, 34.42; H, 2.31; N, 2.90. Both *E* and *Z* isomers were present in a 1:1 ratio (¹H NMR). In solution at room temperature, **10** slowly decomposed into **9** and the smell of HSEt was discernible.

Repeating this reaction with $[(CO)_5W\{C(SPh)Ph\}]$ gave only the nitrile **9** in ca. 80% yield whereas $[(CO)_5W\{C(SPh)Me\}]$ was converted into a 1:1 *E*:*Z* isomeric mixture of the imidate **11**. Filtration of the reaction mixture through SiO_2, concentration to 10 mL, and addition of the same volume of hexane gave only the *Z* isomer (¹H NMR) upon cooling to −40 °C, mp 95–96 °C. Evaporation of solvent and recrystallization of the residue from hexane produced yellow crystals which were shown by ¹H and ¹³C NMR to be the *E* isomer which contained no observable traces of the other isomer, mp 88–90 °C. No conversion of any isomer into the other occurred at room temperature in solution. Anal. (*Z* isomer) Calcd for $C_{13}H_9NO_5SW$: C, 32.86; H, 1.91; N, 2.95. Found: C, 32.71; H, 1.94; N, 2.98.

Aminolysis of the Imidate Complex 1. Dry dimethylamine was slowly bubbled through a solution of $[(CO)_5W\{NH{=}C(OMe)Ph\}]$ (459 mg, 1.0 mmol) in 30 mL of diethyl ether for 10 min. The yellow solution then contained no more starting material, and thin-layer chromatographic monitoring indicated the formation of only one product. After washing through SiO_2 with diethyl ether and stripping of solvent under reduced pressure, yellow microcrystals (383 mg, 81.2%) containing both *E* and *Z* isomers in a ratio of 3:1 was obtained. Recrystallization from diethyl ether–hexane (1:2) gave single crystals of the *E* isomer which were used in a crystal structure study; decomp at 105–108 °C. Anal. (*E*/*Z* mixture) calcd for $C_{14}H_{12}N_2O_5W$: C, 35.61; H, 2.60; N, 6.31. Found: C, 35.64; H, 2.56; N, 6.38.

Crystallographic Analyses. Crystal data for compounds **1** and **13** and details of their structure determinations are given in Table V. Fractional coordinates are given in Table VI. All non-hydrogen atoms were refined with anisotropic temperature factors. All hydrogen atoms were refined in calculated positions, riding at 1.08 Å from the C and N atoms to which they are bonded.

Acknowledgment. We thank the Foundation for Research and Development for financial assistance and the NCRL of the CSIR for the collection of the diffractometer data.

Registry No. (*E*)-**1**, 109011-18-9; (*Z*)-**1**, 109063-26-5; (*E*)-**2**, 109011-19-0; (*Z*)-**2**, 109063-27-6; (*E*)-**3**, 109011-20-3; (*Z*)-**3**, 109063-28-7; **4**, 109011-21-4; **5**, 109011-22-5; **6**, 86011-29-2; **7**, 71175-83-2; **8**, 71175-82-1; **9**, 19705-90-9; (*E*)-**10**, 109011-23-6; (*Z*)-**10**, 109063-29-8; (*E*)-**11**, 109011-24-7; (*Z*)-**11**, 109063-30-1; **12**, 15096-68-1; (*E*)-**13**, 109011-25-8; (*Z*)-**13**, 109063-31-2; A, 67126-34-5; B, 61577-40-0; $W(CO)_5\{C(OMe)Ph\}$, 37823-96-4; $W(CO)_5\{C(OEt)Ph\}$, 36834-98-7; $W(CO)_5\{C(OMe)Me\}$, 20540-70-9; $(CO)_5Cr{=}C(OMe)Ph$, 27436-93-7; $(CO)_5Cr{=}C(OEt)Ph$, 26160-57-6; $(CO)_5W\{C(SEt)Ph\}$, 109011-26-9; $(CO)_5W\{C(SPh)Ph\}$, 78955-18-7; $(CO)_5W\{C(SPh)Me\}$, 52843-33-1; $(CO)_5Cr(SPh_2)$, 65198-74-5; $(CO)_5W(SPh_2)$, 65198-79-0; $(CO)_5Cr(PPh_3)$, 14917-12-5; $(CO)_5W(PPh_3)$, 15444-65-2; NaH, 7646-69-7; NaOEt, 124-41-4; NaSEt, 811-51-8; $(CO)_5Cr$, 13007-92-6; $(CO)_5W$, 14040-11-0; *S*,*S*-diphenylsulfilimine, 36744-90-8.

Supplementary Material Available: Anisotropic thermal parameters (Table A) and calculated hydrogen positions for **1** and **13** (Table B) (3 pages); listings of observed and calculated structure factors for **1** and **13** (Tables C and D) (27 pages). Ordering information is given on any current masthead page.