Organometallics **1997,** *16,* 3863–3866

Carbonylation of Amines with a Tungsten(IV) Carbonyl Complex

Jennifer E. McCusker, Khalil A. Abboud, and Lisa McElwee-White*

Department of Chemistry, University of Florida, Gainesville, Florida 32611

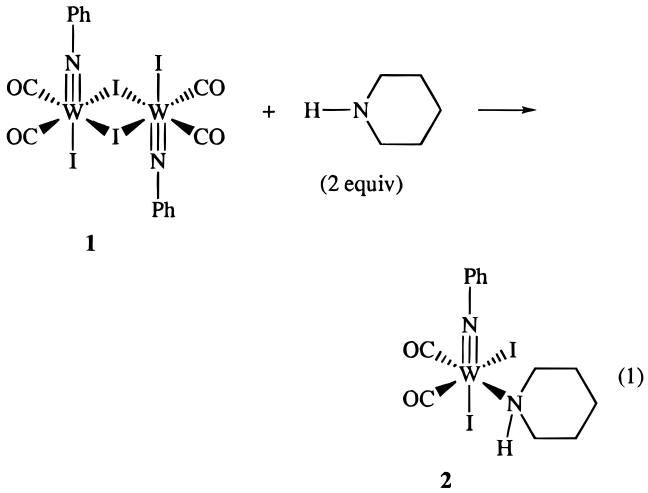
Received May 9, 1997[⊗]

Summary: Reaction of $[(CO)_2W(NPh)I_2]_2$ (**1**) *with 2 equiv of piperidine yielded* $(CO)_2W(NPh)I_2(pip)$. *In the presence of excess amine, secondary amines* (R_2NH) *were carbonylated to the formamides* R_2NCHO *while primary amines* ($R'NH_2$) *were converted to the ureas* $R'NHCONHR'$.

Carbonylation of organic molecules in the presence of transition-metal complexes is a topic of long-standing interest.[1] Amine substrates have attracted much attention,[2] and conversions of amines into formamides,[3] carbamates,[4] ureas,[5] α-keto amides,[6] and lactams[7] have been reported. Early efforts toward the carbonylation of amines focused on nickel, cobalt, and their salts as catalysts.[2] Recognition that the catalytically active species in these systems were probably metal carbonyls led to studies involving Fe,[8] Co,[7a,9] Rh,[4g] Mn,[5b,10,11] Re,[12] and Ru[3,4d,13,14] carbonyl complexes. Although many metal carbonyl catalysts have been examined, amine carbonylation involving group 6 metals[15] remains rare.

Typically, transition-metal-catalyzed amine carbonylation reactions require stringent conditions of high temperature and pressure. Depending on the desired product, addition of a halide source (usually iodide) and/or an oxidant may be necessary. The product distributions depend upon the catalyst and reaction conditions. However, for reactions carried out in the absence of alcohols, there is a general trend in which secondary amines yield formamides while ureas are produced from primary amines.

We recently reported the formation of the iodo-bridged dimer $[(CO)_2W(NPh)I_2]_2$ (**1**) upon oxidation of the zwitterion $(CO)_5WNPhNPhC(OMe)Ph$ with 1 equiv of I_2.[16] Subsequent treatment of dimer **1** with two-electron-donor ligands resulted in the formation of monomeric compounds of the type $(CO)_2I_2W(NPh)L$, where L = THF, CH_3CN, pyridine, NEt_3, or $2,4,6\text{-}Me_3C_6H_2NH_2$. In an effort to extend the series of derivatives, **1** was reacted with secondary and primary aliphatic amines. As shown in eq 1, reaction of **1** with 2 equiv of piperidine yielded $(CO)_2I_2W(NPh)(pip)$ (**2**).



Complex **2** could be identified by comparison of its spectral data to those of similar complexes.[16] As observed with the THF and triethylamine adducts, the ^1H NMR spectrum of complex **2** reflects the chirality of the metal center. The β hydrogens of the piperidine ring are diastereotopic, appearing as well-resolved quartets

---

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

[1] For monographs on the topic, see: (a) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation: Direct Synthesis of Carbonyl Compounds*; Plenum: New York, 1991. (b) Sheldon, R. A. *Chemicals from Synthesis Gas*; Dordrecht: Boston, MA, 1983. (c) Wender, I.; Pino, P. *Organic Syntheses via Metal Carbonyls,* Wiley Interscience: New York, 1968.

[2] Rosenthal, A.; Wender, I. ref 1c, pp 405–466.

[3] (a) Süss-Fink, G.; Langenbahn, M.; Jenke, T. *J. Organomet. Chem.* **1989**, *368*, 103–109. (b) Jenner, G.; Bitsi, G.; Schleiffer, E. *J. Mol. Catal.* **1987**, *39*, 233–236. (c) Bitsi, G.; Jenner, G. *J. Organomet. Chem.* **1987**, *330*, 429–435. (d) Tsuji, Y.; Ohsumi, T.; Kondo, T.; Watanabe, Y. *J. Organomet. Chem.* **1986**, *309*, 333–344.

[4] (a) Valli, V. L. K.; Alper, H. *Organometallics* **1995**, *14*, 80–82. (b) Pri-Bar, I.; Schwartz, J. *J. Org. Chem.* **1995**, *60*, 8124–8125. (c) Hartstock, F. W.; Herrington, D. G.; McMahon, L. B. *Tetrahedron Lett.* **1994**, *35*, 8761–8764. (d) Kanagasabapathy, S.; Gupte, S. P.; Chaudhari, R. V. *Ind. Eng. Chem. Res.* **1994**, *33*, 1–6. (e) Giannocaro, P. *J. Organomet. Chem.* **1994**, *470*, 249–252. (f) Leung, T. W.; Dombek, B. D. *J. Chem. Soc., Chem. Commun.* **1992**, 205–206. (g) Mulla, S. A. R.; Gupte, S. P.; Chaudhari, R. V. *J. Mol. Catal.* **1991**, *67*, L7–L10. (h) Fukuoka, S.; Chono, M.; Kohno, M. *J. Org. Chem.* **1984**, *49*, 1458–1460. (i) Fukuoka, S.; Chono, M.; Kohno, M. *J. Chem. Soc., Chem. Commun.* **1984**, 399–400. (j) Alper, H.; Hartstock, F. W. *J. Chem. Soc., Chem. Commun.* **1985**, 1141–1142.

[5] (a) Giannocaro, P.; Nobile, C. F.; Mastrorilli, P.; Ravasio, N. *J. Organomet. Chem.* **1991**, *419*, 251–258. (b) Srivastava, S. C.; Shrimal, A. K.; Srivastava, A. *J. Organomet. Chem.* **1991**, *414*, 65–69. (c) Bassoli, A.; Rindone, B.; Tollari, S.; Chioccara, F. *J. Mol. Catal.* **1990**, *60*, 41–48. (d) Pri-Bar, I.; Alper, H. *Can. J. Chem.* **1990**, *68*, 1544–1547.

[6] (a) Srivastava, R. S.; Singh, G.; Nakano, M.; Osakada, F.; Yamamoto, A. *J. Organomet. Chem.* **1993**, *451*, 221–229. (b) Huang, L.; Ozawa, F.; Yamamoto, A. *Organometallics* **1990**, *9*, 2603–2611. (c) Alper, H.; Vasapollo, G.; Hartstock, F. W.; Mlekuz, M.; Smith, D. H. J.; Morris, G. E. *Organometallics* **1987**, *6*, 2391–2393.

[7] (a) Piotti, M. E.; Alper, H. *J. Am. Chem. Soc.* **1996**, *118*, 111–116. (b) Campi, E. M.; Chong, J. M.; Jackson, W. R.; Van Der Schoot, M. *Tetrahedron* **1994**, *50*, 2533–2542.

[8] Hieber, W.; Kahlen, N. *Chem. Ber.* **1958**, *91*, 2223–2233.

[9] Sternberg, H. W.; Wender, I.; Friedel, R. A.; Orchin, M. *J. Am. Chem. Soc.* **1953**, *75*, 3148–3151.

[10] Dombek, B. D.; Angelici, R. J. *J. Organomet. Chem.* **1977**, *134*, 203–217.

[11] Calderazzo, F. *Inorg. Chem.* **1965**, *4*, 293–296.

[12] Hieber, W.; Schuster, L. *Z. Anorg. Allg. Chem.* **1956**, *287*, 214–222.

[13] Hieber, W.; Heusinger, H. *J. Inorg. Nucl. Chem.* **1957**, *4*, 179–184.

[14] Byerly, J. J.; Rempel, G. L.; Takebe, N.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1971**, 1482–1483.

[15] (a) Jetz, W.; Angelici, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 3799–3802. (b) Doxsee, K. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7696–7698.

[16] (a) McGowan, P. C.; Massey, S. T.; Abboud, K. A.; McElwee-White, L. *J. Am. Chem. Soc.* **1994**, *116*, 7419–7420. (b) Barnett, N. D. R.; Massey, S. T.; McGowan, P. C.; Wild, J. J.; Abboud, K. A.; McElwee-White, L. *Organometallics* **1996**, *15*, 424–428.

S0276-7333(97)00388-9 CCC: $14.00

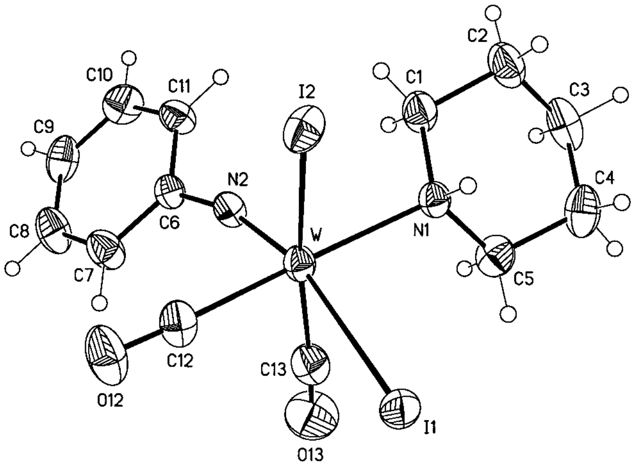


Figure 1. Thermal ellipsoids drawing of compound **2** showing the crystallographic numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. Selected distances (Å) and angles (deg) are as follows: W−N1 2.249(3), W−N2 1.764(3), W−C13 2.036(5), W−C12 2.053(4), W−I1 2.836(1), W−I2 2.794(1), W−N1−C1 111.7(2), W−N2−C6 164.9(3), N1−W−N2 100.6(1), C1−N1−C5 109.4(3).

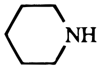
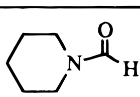
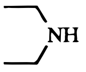
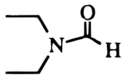
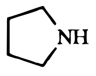
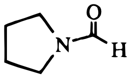
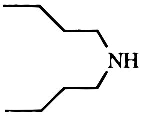
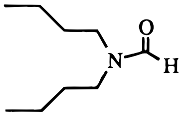
Table 1. Crystal Data and Structure Refinement for 2

empirical formula	$C_{13}H_{16}I_2N_2O_2W$
fw	669.93
temperature	173(2) K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimensions	$a = 8.9583(3)$ Å $b = 20.6165(5)$ Å $c = 10.0082(3)$ Å $\beta = 103.22°$
volume, Z	1799.41(9) A^3, 4
density calcd	2.473 Mg/m^3
abs coeff	9.853 mm^{-1}
$F(000)$	1216
cryst size	0.06 × 0.11 × 0.21 mm
θ range	1.98−27.50°
limiting indices	$-11 \leq h \leq 12, -24 \leq k \leq 27, -11 \leq l \leq 13$
no. of reflns collected	12134
no. of independent reflns	4105 [R(int) = 0.0284]
abs corr	empirical
min, max transmission	0.415, 0.853
refinement method	full-matrix least-squares on F^2
data/restraints/params	4099/0/182
goodness-of-fit on F^2	1.010
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0229$, $wR_2 = 0.0483$ [3526]
R indices (all data)	$R_1 = 0.0312$, $wR_2 = 0.0514$
ext coeff	0.00067(6)
largest diff peak and hole	1.359 and −0.843 e A^{-3}

at 3.15 and 2.75 ppm. The NH proton is seen as a broad singlet at 4.34 ppm. The ^{13}C NMR spectrum of **2** exhibits two inequivalent carbonyl signals, which allows the assignment of the carbonyl ligands as *cis*. Additional evidence for the stereochemistry at the metal can be found in the two IR stretches for the *cis*-carbonyl ligands. Confirmation of the structural assignment was obtained by X-ray crystallography (Table 1), and a thermal ellipsoids drawing of **2** appears in Figure 1.

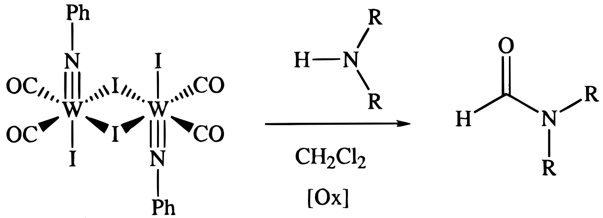
In contrast to the smooth conversion of **1** to **2** in the presence of 2 equiv of piperidine, treatment of a methylene chloride solution of dimer **1** with 10 equiv of piperidine under nitrogen resulted in a very complex reaction mixture. After exposure to air, the solution turned from magenta to banana-yellow, producing 1-formylpiperidine, aniline, piperidine hydroiodide, and several unidentified components. GC analysis of the oxidized reaction mixtures established that 1-formylpiperidine had been obtained in 36% yield per tungsten atom.

Table 2. Carbonylation of Secondary Amines to Formamides

Amine	Product	% Yield[a,b]
		36
		8
		61
		20

[a] Calculated per equivalent of tungsten. [b] Determined by GC.

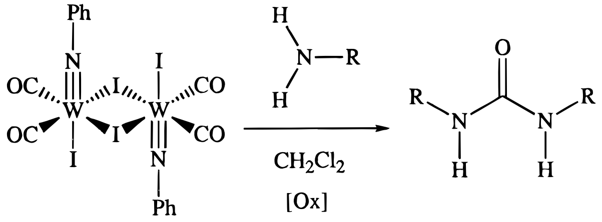
Experiments with other secondary amines established that carbonylation to formamides using dimer **1** is a general reaction (eq 2). The results for a series of secondary amines are shown in Table 2. The GC yields, reported on a per tungsten basis, vary from 61% for pyrrolidine formamide to 8% for diethyl formamide. The low yield of diethyl formamide can be attributed to loss during the oxidation and work-up procedures. Within the limits of detection, the carbonylation of secondary amines is selective for formamides. Despite literature precedent for formation of ureas[5] and α-keto amides[6] from amines, these species were not observed in the reaction mixtures.



1

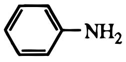
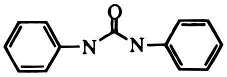
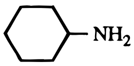
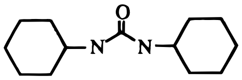
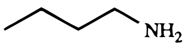
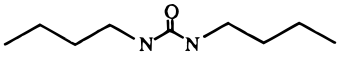
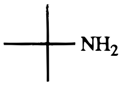
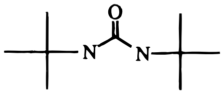
(2)

However, reaction of **1** with primary amines produced a different result. Under the same reaction conditions, primary amines were selectively carbonylated to the corresponding 1,3-disubstituted ureas (eq 3). No other carbonylation products could be detected, although aniline and the amine hydroiodides could be observed in the ^1H NMR spectra of the reaction mixtures. The results for a series of primary amines are shown in



(3)

Table 3. Carbonylation of Primary Amines to Ureas

Amine	Product	% Yield[a,b]
		105
		57
		56
		67

[a] Calculated per equivalent of tungsten. [b] Isolated yields.

Table 3. The isolated yields per tungsten vary from 56% for di-*n*-butylurea to 105% for diphenylurea.[17]

This reaction exhibits some similarities to other systems known to catalyze the carbonylation of amines. For example, use of iodide complexes or addition of iodide promoters is common in the literature, especially in the Pd-catalyzed conversion of amines to carbamates. Complex **1** contains iodides as ancillary ligands. However, amine carbonylation by **1** is performed at room temperature under N_2 followed by oxidation with air at ambient pressure. In contrast, most of the previously reported carbonylation conditions involve elevated temperatures and high pressures of CO or CO/O_2 mixtures. Room temperature reaction is possible in this system because dimer **1** is in equilibrium with the corresponding monomer in solution,[16b] providing an open coordination site where the incoming amine can bind without the need to dissociate a ligand. CO pressure is not required because the reaction utilizes existing carbonyl ligands. Clearly, development of a catalytic variant would require additional CO.

Although there has not been an extensive mechanistic study, some information has been obtained. Conversion of dimer **1** to the monomeric amine complex $(CO)_2I_2W(NPh)(amine)$ is undoubtedly the first step of these reactions. Piperidine complex **2** has been structurally characterized, and we have spectroscopic evidence for the formation of analogous complexes with primary amines. There is also spectroscopic evidence for the formation of carbamoyl complexes in the reactions of **1** with both secondary and primary amines. Carbamoyl intermediates have precedent in the carbonylation of CH_3NH_2 by $[(\eta^5\text{-}C_5H_5)W(CO)_4]PF_6$,[15a] for which the first step is conversion of $[(\eta^5\text{-}C_5H_5)W(CO)_4]^+$ to the carbamoyl complex $(\eta^5\text{-}C_5H_5)W(CO)_3(CONHCH_3)$ upon reaction with 2 equiv of CH_3NH_2. According to the criteria formulated by Angelici,[18] the carbonyl stretching frequency of 2066 cm^{-1} for **2** renders it likely to form carbamoyl complexes by nucleophilic attack of amines on a carbonyl. IR spectra of unoxidized reaction mixtures of **1** with piperidine exhibited a stretch at 1574 cm^{-1}, while **1** with n-butylamine exhibited a stretch at 1589 cm^{-1}. These values are consistent with those reported for carbamoyl complexes.[18]

In summary, we have developed a method to stoichiometrically carbonylate primary and secondary amines using dimer **1**. This is a rare example of carbonylation using a group 6 metal complex. The reaction not only proceeds under very mild conditions but is selective as well. Primary amines produce ureas, while secondary amines yield formamides. Further work aimed at elucidation of the mechanism and broadening the scope of this reaction is currently in progress.

Experimental Section

General. Standard inert atmosphere Schlenk, cannula, and glovebox techniques and freshly distilled solvents were used in all experiments unless stated otherwise. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone. Methylene chloride and hexane were distilled over calcium hydride. All NMR solvents were degassed by three freeze−pump−thaw cycles, then stored in an inert-atmosphere glovebox over 3 Å molecular sieves. All other chemicals were purchased in reagent grade and used with no further purification unless stated otherwise. Authentic samples of the formamides were purchased from Aldrich. Authentic samples of the ureas were prepared from the corresponding amines and isocyanates.[19]

^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 or a General Electric QE 300 spectrometer. IR spectra were recorded on a Perkin-Elmer 1600 FTIR. GC was performed on an HP5890 chromatograph containing a 15 m × 0.32 mm column of AT-WAX on fused silica or on a Varian 3500 chromatograph containing a J & W fused silica capillary column (DB-5-30W; film thickness 0.25 μm). High-resolution mass spectrometry was performed by the University of Florida analytical service.

Synthesis of $(CO)_2I_2W(NPh)(pip)$ (2). To a stirred solution of dimer **1** (170 mg, 0.146 mmol) in 15 mL of CH_2Cl_2 was added 2 equiv of piperidine (0.028 mL, 0.292 mmol). A color change from red to purple occurred immediately. After 5 min of stirring, the CH_2Cl_2 was removed under vacuum. The resulting oil was taken up in 10 mL of Et_2O and cannulated away from any insoluble particles. Hexane (5 mL) was added, and the solution was placed in a −40 °C freezer overnight. Complex **2** was collected as a dark purple powder (162 mg, 83% yield). X-ray quality crystals were grown from a 50:50 mixture of Et_2O and hexane. ^1H NMR ($CDCl_3$): δ 7.4−7.1 (m, 5H), 4.33 (s, 1H), 3.15 (q, 2H), 2.75 (q, 2H), 1.87−1.47 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 209.8, 207.8, 153.2, 129.6, 129.1, 125.1, 59.1, 56.7, 28.9, 28.8, 23.1. IR (CH_2Cl_2): ν_{CO} 2066, 1987 cm^{-1}. HRMS (FAB): 641.9025 $(M - CO)^+$, calcd 641.9175.

Carbonylation of Secondary Amines with 1. The following procedure is typical: To a stirred solution of dimer **1** (100 mg, 0.086 mmol) in 5 mL of CH_2Cl_2 was added 10 equiv of piperidine (73 mg, 0.86 mmol). A color change from red to purple occurred immediately. The solution was stirred under N_2 for 30 min, then opened to air for 24 h, during which the solution slowly turned from purple to yellow. The solution was then filtered through a small pad of Celite. The organic product was identified as 1-formylpiperidine by comparison to an authentic sample. Its yield was determined by GC analysis of the solution to be 7 mg (36% yield).

Carbonylation of Primary Amines with 1. The following procedure is typical: To a stirred solution of dimer **1** (110 mg, 0.095 mmol) in 5 mL of CH_2Cl_2 was added 10 equiv of aniline (0.086 mL, 0.95 mmol). A color change from red to purple occurred immediately. The solution was stirred under N_2 for 30 min, then opened to air for 24 h, during which the solution slowly turned from purple to dark orange and a white solid precipitated out. The precipitate was collected and rinsed

---

(17) Note that since each tungsten atom bears two carbonyls, the theoretical yield of urea is 200% if all of the CO is consumed during the carbonylation reaction.

(18) Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335−341.

(19) For a review on synthesis of ureas, see: Vishnyakova, T. P.; Golubeva, I. A.; Glebova, E. V. *Russ. Chem. Rev.* **1985**, *54*, 249−261.

with 2 × 10 mL of CH_2Cl_2 to obtain a white solid (42.3 mg, 105%). The solid was identified as diphenylurea by comparison to an authentic sample.

Experimental Procedure for X-ray Crystallography. Data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Cell parameters were refined using up to 8192 reflections. A hemisphere of data (1381 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was <1%). ψ scan absorption corrections were applied based on the entire data set.

The structure was solved by the direct methods in *SHELXTL5*[20] and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. There were 182 parameters refined in the final cycle of refinement using 3526 reflections with $I > 2\sigma(I)$ to yield $R_1 = 2.29\%$ and $wR_2 = 4.83\%$, respectively. Refinement was done using F^2.

Acknowledgment. Funding for this research was provided by the Office of Naval Research. K.A.A. wishes to acknowledge the National Science Foundation and the University of Florida for funding the purchase of the X-ray equipment.

Supporting Information Available: Tables of crystal data and structure refinement, bond distances, bond angles, positional parameters, and anisotropic displacement parameters for **2** (6 pages). Ordering information is given on any current masthead page.

OM970388F

---

[20] Sheldrick, G. M. *SHELXTL5*; Siemens Analytical Instrumentation: Madison, WI, 1995.

Additions and Corrections

1995, Volume 14

Richard D. Adams* and Stephen B. Falloon: Catalytic Cyclooligomerization of Thietane by Dirhenium Carbonyl Complexes.

Page 1748. The minor fraction, identified in this report as 1,5,9,13,17,21-hexathiacyclotetracosane, 24S6, has now been analyzed for molecular weight by gel permeation chromatography. This analysis indicates that the fraction is composed principally (>95%) of a range of low-molecular-weight polymers with an average $\bar{M}_w$ value of 8703, a number average molecular weight of $\bar{M}_n = 5106$, and a polydispersity of 1.7. Except for the difference in molecular weights, these polymers are virtually identical spectroscopically and analytically with 24S6. We wish to thank J. L. Perrin and A. M. Rawlett (Department of Chemistry and Biochemistry, University of South Carolina) for discovering this error.