ORGANOMETALLICS

Clusters as ligands. Stabilization of a cadmium-cobalt Cd3Co core in [.mu.3-Co(CO)3]Cd3{.mu.-[(CO)9Co3(.mu.3-CCO2)]}3(THF)3

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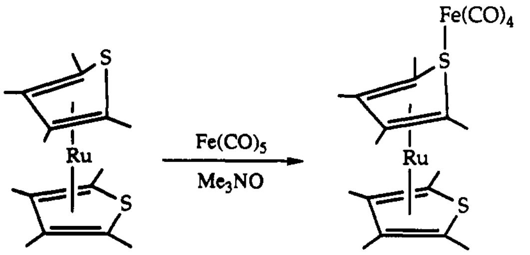
The assignment of 1 as Ru(η^4-C_4Me_4S)(η^5-C_4Me_4S) is supported by the synthesis of its brown-orange, thermally stable $Fe(CO)_4$ adduct (eq 3). The 400-MHz ^1H NMR spectrum (20 °C) of 1·$Fe(CO)_4$ showed four equally intense singlets, as expected for a static structure.[12] The average of ^{13}C NMR chemical shifts for 1·$Fe(CO)_4$ corresponds to those seen for 1.



(3)

The crystallographic study confirmed that 1·$Fe(CO)_4$ is described as (η^5-C_4Me_4S)Ru{η^4:η^1-C_4Me_4S($Fe(CO)_4$)}, which adopts a symmetric structure with an approximate symmetry plane containing atoms Ru, Fe, S(1), and S(2) (Figure 1).[13] The two pairs of C=C groups are nearly eclipsed, as are the iron, two sulfur atoms, and one CO. The η^5-C_4Me_4S ring and the diene portion of the η^4:η^1-C_4Me_4S are nearly mutually parallel with a dihedral angle of only 1.5°. The slightly shorter Ru–C distances for the η^4:η^1-C_4Me_4S portion of the molecule suggests that this ligand is the better electron acceptor. For the η^4:η^1-C_4Me_4S ligand the S atom is bent out of the diene-like plane with a dihedral angle (between C10–C13 and C10–S2–C13) of 32.1°.[14]

In summary, we have succeeded in isolation of the thiophene analogue of Fischer's classic Ru(η^4-C_6Me_6)(η^6-C_6Me_6).[15] The new species differs from the hexamethylbenzene complex in that it is highly fluxional and unstable thermally. Its fluxional character is indicative of the increased pliability of heterocyclic ligands. Its instability is almost certainly related to the decomposition of thiophenes on Ru surfaces even at 120 K[3] and possibly the metal-catalyzed desulfurization of thiophenes.[16] Further studies are underway on the reactivity of 1 and related Ru(0) thiophene complexes.

Acknowledgment. This research was supported by the U.S. Department of Energy through Contract No. DOE-DEFG02-90ER14146. S.L. acknowledges receipt of a graduate fellowship from the University of Illinois. Ruthenium was obtained on loan from Johnson Matthey.

Supplementary Material Available: For 1·$Fe(CO)_4$, tables of crystal parameters and intensity collection data, bond distances and angles, and positional and thermal parameters (7 pages). Ordering information is given on any current masthead page.

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[11] The following resonance energy values for the π-ligands discussed herein are given in the literature (kJ/mol): C_6H_6 (150);[11a] C_6Me_6 (109–138);[11b] C_4H_4S (84–121).[11a] (a) Cook, M. J.; Katritzky, A. R.; Linda, P. *Adv. Heterocycl. Chem.* **1974**, *17*, 255. (b) Wheland, G. W. *Resonance in Organic Chemistry*; Wiley: New York, 1955; p 98.

[12] A THF solution of 1, prepared from 170 mg (0.250 mmol) of $[Ru(C_4Me_4S)_2](OTf)_2$ with 97.5 mg (0.516 mmol) of Cp_2Co at −78 °C, was treated with 59.6 mg (0.304 mmol) of $Fe(CO)_5$ and 20.6 mg (0.274 mmol) of Me_3NO. After 4 h, the yellow solution was warmed to room temperature and evaporated and the residue extracted with toluene. Evaporation of the toluene extract afforded 114 mg of brown-orange crystals (83% based on $[Ru(C_4Me_4S)_2](OTf)_2$). Anal. Found (calcd) for $C_{20}H_{24}FeO_4RuS_2$: C, 43.78 (43.72); H, 4.48 (4.40); S, 11.66 (11.67). ^1H NMR (400 MHz, C_6D_6, 20 °C): 1.51, 1.48, 1.25, 0.95 ppm. ^{13}C NMR (100 MHz, C_6D_6, 20 °C): 217.20, 96.24, 89.42, 83.44, 54.90, 14.04, 12.75, 12.25, 10.41 ppm. FDMS: *m/e* 550 (M^+ for ^{102}Ru and ^{56}Fe). IR (KBr, ν_{CO}): 2014 (s), 1980 (m), 1923 (s), 1903 (s) cm^{-1}.

[13] Crystals of 1·$Fe(CO)_4$ were grown from toluene: Syntex $P2_1$, Mo Kα, numerical adsorption correction; ω scan; Ru, Fe, S, O, and C anisotropic; lattice constants (253 K) a = 1056.4 (2) pm, b = 1267.5 (3) pm, c = 1708.8 (8) pm, $\alpha = \beta = \gamma = 90°$, $V = 2288 \times 10^6$ pm^3; orthorhombic, $P2_12_12_1$ (No. 19); Z = 4; μ(Mo Kα) = 14.78 cm^{-1}; profile analysis $2\theta_{max}$ = 50.0°, 2228 reflections, 2111 with $I > 2.58\sigma(I)$, 349 parameters, R = 0.030, R_w = 0.039.

[14] As described in ref 2, several examples of η^4:η^1-C_4R_4S complexes are known; recent reports: Luo, S.; Ogilvy, A. E.; Rheingold, A. L.; Wilson, S. R. *Organometallics* **1991**, *10*, 1002. Choi, M.-G.; Angelici, R. J. *Organometallics* **1991**, *10*, 2438.

[15] Fischer, E. O.; Elschenbroich, C. *Chem. Ber.* **1970**, *103*, 162. $Ru(C_6H_6)_2$, characterized only by ^1H NMR spectroscopy, decomposes below 0 °C to give a "brown solid": Timms, P. L.; King, R. B. *J. Chem. Soc., Chem. Commun.* **1978**, 898.

[16] Gates, B. C. *Catalytic Chemistry*; Wiley: New York, 1991. Reynolds, J. G. *Chem. Ind.* **1991**, 570.

Clusters as Ligands. Stabilization of a Cd_3Co Core in $[\mu_3\text{-}Co(CO)_3]Cd_3\{\mu\text{-}[(CO)_9Co_3(\mu_3\text{-}CCO_2)]\}_3(THF)_3$

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Summary: The reaction of the cluster ligand precursor $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ with $Cd(CH_3)_2$ yields $[\mu_3\text{-}Co(CO)_3]Cd_3\{\mu\text{-}[(CO)_9Co_3(\mu_3\text{-}CCO_2)]\}_3(THF)_3$, 1, as one of the reaction products. Crystallographic characterization shows a triangular Cd_3 core capped with a $Co(CO)_3$ fragment and edge-bridged with three cluster carboxylate ligands. The presence or absence of a Cd–Cd bond is subject to interpretation. It is argued that the most reasonable description of the cadmium centers is as Cd^+.

We have pointed out the advantages of considering a transition metal cluster as a bulky substituent with unusual electronic properties.[1] In principle, joining a transition metal cluster to a ligand functionality permits the construction of clusters of clusters based on established coordination geometries of cationic metal centers. Our work to date based on this idea also demonstrates that a cluster substituent can significantly change the character of the ligand functionality. Thus, the direct, facile low-temperature formation of $Zn_4O\{\mu\text{-}[(CO)_9Co_3(\mu_3\text{-}CCO_2)]\}_6$[2] and the fast, clean exchange of $(CO)_9Co_3(\mu_3\text{-}CCOOH)$ for acetate in $Mo_2(MeCOO)_4$[3] were unforeseen but can be explained

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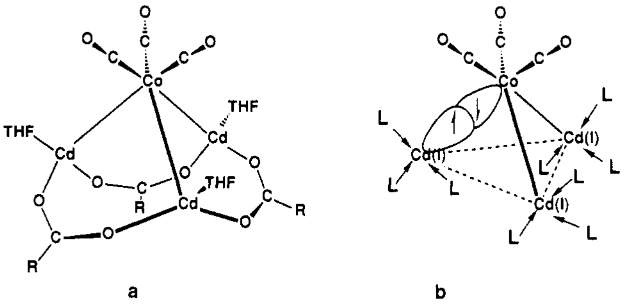
[1] Meng, X.; Rath, N. P.; Fehlner, T. P.; Rheingold, A. L. *Organometallics* **1991**, *10*, 1986.

[2] Cen, W.; Haller, K. J.; Fehlner, T. P. *Inorg. Chem.* **1991**, *30*, 3120.

[3] Cen, W.; Lindenfeld, P.; Fehlner, T. P. *J. Am. Chem. Soc.* **1992**, *114*, 5451.

Chart I



R = $(CO)_9Co_3C$

in terms of the nature of the electronic coupling of the $(CO)_9Co_3(\mu_3\text{-}C)$ cluster fragment with the carboxylate functionality.[4] In contrast to these substituent effects on the kinetics and mechanisms of coordination, herein we present an example of a compound in which the ligand $[(CO)_9Co_3(\mu_3\text{-}CCO_2)]^-$ plays a structural role in the stabilization of an unusual inorganometallic[5] compound containing formal Cd(I).

The slow addition of 1 equiv of $CdMe_2$ (1 M in hexane) to 1 equiv of $(CO)_9Co_3(\mu_3\text{-}CCOOH)$ in THF at room temperature gives a homogeneous purple-brown solution. After reduction of the volume and addition of toluene, the reaction mixture was heated for 3 h at 70 °C. Filtration and crystallization at −20 °C resulted in the formation of large (0.3–1.0 mm), parallelpiped black crystals (**1**) mixed with fine, fragile pink-brown particles (<0.1 mm). Washing with toluene to remove the byproduct resulted in a yield of **1** of 40% based on the cluster ligand.[6] A section of one of the large crystals was of X-ray quality, and the composition and structure of **1** as defined by the diffraction experiment[7] is shown in Figure 1.

The essential features of the structure of **1**, $[\mu_3\text{-}Co(CO)_3]Cd_3\{\mu\text{-}[(CO)_9Co_3(\mu_3\text{-}CCO_2)]\}_3(THF)_3$, are given in Chart Ia. The neutral compound consists of an equilateral triangle of Cd atoms (average d_{Cd-Cd} = 2.980 (3) Å) capped with a $Co(CO)_3$ fragment (average d_{Cd-Co} = 2.573 (7) Å) with the Cd–Cd edges bridged by $[(CO)_9Co_3(\mu_3\text{-}CCO_2)]^-$ ligands. Each Cd atom is also coordinated to a molecule of THF. The Cd–Co distances are larger than the Zn–Co distances in $[(CO)_4CoZn]_2$ (2.48 Å)[8] but similar to the Hg–Co distances in $Hg_9Co_6(CO)_{18}$ (2.57 Å).[9] Clearly these are bonding. On the other hand, the observed Cd–Cd distance in **1** is close to that in cadmium metal (3.04 Å) but lies midway between that of a Cd–Cd bond (2.576 Å in Cd_2^{2+})[10] and that between bridged but nonbonded Cd–Cd centers (3.452 Å in $Cd_2(F_3CCO_2)_4(PPh_3)_2$).[11] On the basis of the structural metrics, it is a moot question whether the Cd centers in **1** should be considered to be bonded to each other. Curiously, the environment of each Cd center is roughly octahedral and similar to that of a $M(CO)_3$ fragment in a capped $\mu_3\text{-}EM_3(CO)_9$ cluster[12] in which M–M bonding is an accepted feature of the electronic structure.

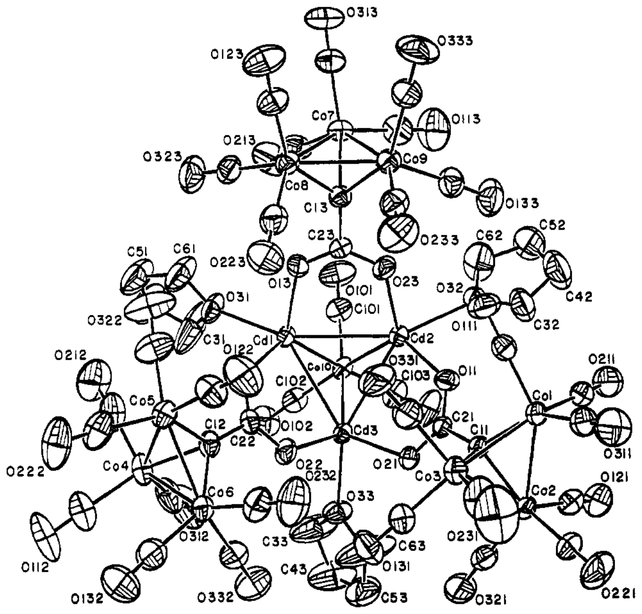


Figure 1. ORTEP drawing of $[\mu_3\text{-}Co(CO)_3]Cd_3\{\mu\text{-}[(CO)_9Co_3(\mu_3\text{-}CCO_2)]\}_3(THF)_3$ indicating the atom numbering scheme. Thermal ellipsoids are drawn to illustrate 30% probability surfaces. Hydrogen atoms are omitted for clarity.

At the level of counting electrons there are two reasonable ways of formulating this compound. Taking the carboxylate clusters as ligands with a charge of −1, the core fragment, $Cd_3Co(CO)_3$, has an overall charge of +3. Assuming that the $Co(CO)_3$ fragment is neutral, the Cd atoms have a formal oxidation state of I whereas assuming a $[Co(CO)_3]^{3-}$ fragment yields a Cd oxidation state of II. Of course, both are correct and many will prefer the latter, but the interesting question is which is a more realistic expression of the charge on the Cd centers. It is particularly interesting, as $Cd_2(AlCl_4)_2$ is the only structurally characterized compound containing Cd(I).[10]

The CO stretching frequencies provide one means of assessing the charge on the apical metal fragment as well as that on the cobalt atoms of the tricobalt cluster ligands. In addition to the bands expected for the latter, three resolved bands at lower frequencies (1984, 1925, 1915 cm^{-1}) can be assigned to the $Co(CO)_3$ fragment. Ellis has reported the terminal frequencies of $[Co(CO)_3]^{3-}$ (1744, 1600 cm^{-1}),[13] and in $[As_7Cr(CO)_3]^{3-}$ the metal carbonyl fragment is formulated as the dianion and exhibits bands at 1823, 1742, and 1706 cm^{-1}.[14] These observations rule out a large negative charge on the capping $Co(CO)_3$ fragment of **1**. The frequency of the A_1 symmetry stretching mode of the tricobalt alkylidyne cluster is known to correlate with the donor–acceptor ability of the functionality attached to the carbyne carbon. Compared to that observed for the Zn(II) and Co(II) complexes of $[(CO)_9Co_3(\mu_3\text{-}CCO_2)]^-$ character-

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[4] Cen, W.; Haller, K. J.; Fehlner, T. P. *Organometallics*, in press.

[5] *Inorganometallic Chemistry*; Fehlner, T. P., Ed.; Plenum: New York, 1992.

[6] Elemental analysis of the compound was not satisfactory. However, positive ion FAB mass spectrum exhibits as parent ion cluster centered at *m/e* 2052.4 and a half-width of ≈6 amu. Calcd for $^{12}C_{48}{}^{1}H_{24}{}^{112}Cd_3{}^{59}Co_{10}{}^{16}O_{39}$: *m/e* 2150.

[7] Crystal data for $C_{48}H_{24}Cd_3Co_{10}O_{39}$, **1**: space group triclinic $P\bar{1}$ (No. 2), a = 12.615 (1) Å, b = 12.690 (2) Å, c = 25.487 (2) Å, α = 100.04 (1)°, β = 90.33 (1)°, γ = 117.60 (1)°, V = 3542.5 (15) Å^3, d(calcd) = 2.02 g/cm^3, MW 2151.23, Z = 2. Data were collected on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal monochromated Mo Kα source. The structure was solved by direct methods. Full-matrix least-squares refinement for 12651 reflections [$F_o > 3\sigma(F_o)$] of 19377 unique reflections collected over the range $3.0 \leq 2\theta \leq 58.7$ converged with R_1 = 4.5% and R_2 = 4.8%.

[8] Burlitch, J. M.; Hayes, S. E.; Lemley, J. T. *Organometallics* **1985**, *4*, 167.

[9] Ragosta, J. M.; Burlitch, J. M. *Organometallics* **1988**, *7*, 1469.

[10] Faggiani, R.; Gillespie, R. J.; Vekris, J. E. *J. Chem. Soc., Chem. Commun.* **1986**, 517.

[11] Allman, T.; Goel, R. C.; Jha, N. K.; Beauchamp, A. L. *Inorg. Chem.* **1984**, *23*, 914.

[12] Lynam, M. M.; Chipman, D. M.; Barreto, R. D.; Fehlner, T. P. *Organometallics* **1987**, *6*, 2405.

[13] Ellis, J. E.; Barger, P. T.; Winzenburg, M. L. *J. Chem. Soc., Chem. Commun.* **1977**, 686.

[14] Eichhorn, B. W.; Haushalter, R. C.; Huffman, J. C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1032.

ized previously[2,4,15] the A_1 mode of 1 is 2.5 cm^{-1} lower in energy. Although small, this difference corroborates the suggestion that the Cd centers of 1 are more electron rich than would be expected for Cd^{2+}.

Hence, the bonding can be formulated as shown in Chart Ib. An appropriately hybridized Cd^+ coordinated to three Lewis bases has a single remaining valence function containing one electron. The $Co(CO)_3$ fragment is isolobal with CH and can form three two-center two-electron bonds to the individual Cd^+ centers. This model assumes no direct Cd–Cd bonding. Note that for a neutral ligand L, LCd^+ is analogous to LAu and the question of direct Cd–Cd bonding in 1 is similar to that posed by compounds containing adjacent LAu fragments.[16]

One of the drawbacks of metal clusters as substituents is their relatively fragile framework and the consequent necessity of working under conditions in which the cluster does not degrade. It is amusing then to note that this drawback is an advantage here; i.e., $(CO)_9Co_3(\mu_3\text{-}CCOOH)$ serves not only as a source for the ligands that bridge the Cd–Cd edges but also as a thermal source of the $Co(CO)_3$ metal fragment that caps the Cd_3 triangle.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged. W.C. thanks the department for a Reilly Fellowship.

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, anisotropic thermal parameters, and fractional coordinates for hydrogen atoms (12 pages). Ordering information is given on any current masthead page.

OM9203035

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[15] Sturgeon, R. L.; Olmstead, M. M.; Schore, N. E. *Organometallics* 1991, *10*, 1649.

[16] Alvarez, S.; Rossell, O.; Seco, M.; Valls, J.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* 1991, *10*, 2309.

(η^1-Cp)Tc(NAr)$_3$: Synthesis and Structure

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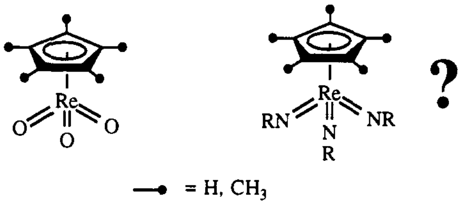
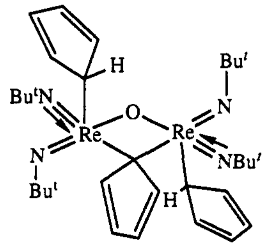
Summary: The reaction of KCp with $TcI(NAr)_3$ (Ar = 2,6-diisopropylphenyl) rapidly forms $(\eta^1\text{-}Cp)Tc(NAr)_3$. A single-crystal X-ray determination confirmed the η^1 nature of the cyclopentadienyl ligand. When $TcI(NAr)_3$ is treated with an excess of KCp, a second cyclopentadienyl group is added to the metal, giving $K[Cp_2Tc(NAr)_3]$.

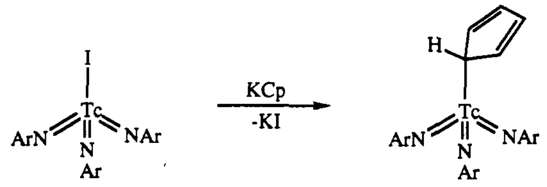
Synthetic procedures for the synthesis of Cp^*ReO_3 and other derivatives (i.e. $CpReO_3$, $(C_5Me_4Et)ReO_3$, and $(C_5H_4Me)ReO_3$) are well established.[1] This, however, is not the case for the analogous imido complexes. In fact, two separate research groups have reported unsuccessful attempts to form complexes of the type $(C_5R_5)Re(NR)_3$:



Herrmann et al. reported several attempts to react $(Me_3SiO)Re(NBu^t)_3$ with a variety of cyclopentadienyl (NaCp, TlCp, $CpSnBu_3$) and pentamethylcyclopentadienyl (KCp*, Cp*MgCl, LiCp*) sources. All attempts failed to give the desired tris(imido)cyclopentadienylrhenium product, and in most cases no reaction was observed. It was thought that reacting bulky ring-transfer reagents with such a highly sterically hindered $(Me_3SiO)Re(NBu^t)_3$ may be preventing these reactions from taking their desired course.[2] Wilkinson and co-workers, using a less encumbered metal complex, obtained more encouraging results. Treatment of $ReCl(NBu^t)_3$ with NaCp resulted in a facile reaction and the eventual isolation of the oxo-bridged dimer.[3]



Scheme I. Synthesis of (η^1-Cp)Tc(NAr)$_3$[a]



[a] Ar = 2,6-diisopropylphenyl.

When a THF solution of $TcI(NAr)_3$[4] is treated with 1 equiv of KCp, a rapid reaction occurs, forming $CpTc(NAr)_3$ and KI (Scheme I). The ^1H NMR spectrum of the reaction mixture is consistent with the formation of $CpTc(NAr)_3$ in near-quantitative yield.[5] This green complex

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[1] (a) Herrmann, W. A.; Serrano, R.; Bock, H. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 383. (b) Klahn-Oliva, A. H.; Sutton, D. *Organometallics* 1984, *3*, 1313. (c) Herrmann, W. A.; Taillefer, M.; de Méric de Bellefon, C.; Behm, J. *Inorg. Chem.* 1991, *30*, 3247–3248. (d) Herrmann, W. A.; Herdtweck, E.; Flöel, M.; Kulpe, J.; Küsthardt, U.; Okuda, J. *Polyhedron* 1987, *6*, 1165–1182. (e) Herrmann, W. A. *J. Organomet. Chem.* 1986, *300*, 111. (f) Herrmann, W. A.; Kiprof, P.; Rypdal, K.; Tremmel, J.; Blom, R.; Alberto, R.; Behm, J.; Albach, R. W.; Bock, H.; Solouki, B.; Mink, J.; Lichtenberger, D.; Gruhn, N. E. *J. Am. Chem. Soc.* 1991, *113*, 6527–6537.

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[3] (a) Danopoulos, A. A.; Wilkinson, G.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* 1991, 181–182. (b) Saboonchian, V.; Danopoulos, A. A.; Gutierrez, A.; Wilkinson, G.; Williams, D. J. *Polyhedron* 1991, *10*, 2241–2253.

[4] Bryan, J. C.; Burns, C. J.; Sattelberger, A. P. *Isotope and Nuclear Chemistry Division Annual Report FY 1990*; Report No. LA-12143-PR; National Technical Information Service, U.S. Department of Commerce: Washington, DC, 1990; pp 40–41.

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