Table I. ^{13}C NMR Spectral Data for Heptamethylindenyl Complexes of Lanthanum Chloride and Related Derivatives of Heptamethylindene[a]

compd	C(9), C(8)	C(2)	C(7), C(4), C(5), C(6)	C(1), C(3)	$CH_3(4)$, $CH_3(7)$, $CH_3(5)$, $CH_3(6)$	$CH_3(3)$, $CH_3(1)$	$CH_3(2)$
Hmi-H	144.5, 141.6	140.3	131.9, 129.9, 127.3, 125.5	46.0, 132.6	15.7, 15.4, 15.2	14.4, 11.2	15.1
KHmi	123.8	122.9	121.0, 116.8	95.8	16.7, 15.6	13.9	10.7
$La(Hmi)_3$[b]	129.5	124.5	124.4, 124.1	106.3	16.8, 15.6	13.3	10.1
$La(Hmi)_2Cl$[b]	131.0	127.0	124.9, 124.6	107.4	16.9, 15.6	13.8	11.2
$La(Hmi)Cl_2$[b,c]	131.5	127.9	125.7, 125.6	109.0	16.8, 15.6	14.3	11.3

[a] Spectra recorded using THF as solvent and C_6D_6 as internal lock. Chemical shifts referenced to THF (β) = 25.3. Peak assignments are based on the numbering scheme shown in reaction 1. [b] The spectrum of this compound containing a CD_3 group at C(3) was virtually identical with the nondeuterated species ($\Delta\delta < 0.4$) except for the relative intensity of the $CH_3(1)$, $CH_3(3)$ resonance. [c] This spectrum contained peaks due to 1a and 3a.

all contained <0.5 % chlorine, indicating that KCl was not an impurity in these samples. No significant amount of K was found in **1**, **2**, or **3** using a flame test. In the case of **2a** ^{13}C NMR spectroscopy showed the presence of **1a**, **2a**, and **3a**. Although giving correct analyses, **2b** and **2c** may be similarly contaminated. These complexes are stable as solutions in THF containing 10% benzene-d_6 for up to 1 month at 25 °C as judged by NMR studies of **1a**, **2a**, and **3a**. These complexes were all soluble to the extent of ca. 0.3 M in THF, ether, and hexamethylphosphoramide but were only sparingly soluble in benzene, cyclohexane, and other hydrocarbon solvents. These complexes were unstable in CS_2, alcohols, ketones, and Me_2SO and are very sensitive to oxygen and moisture. Heptamethylindene was typically seen as a minor component of spectroscopic samples and may have resulted either from adventitious hydrolysis or may have been formed as a byproduct (e.g., by reduction of $LnCl_3$ by KHmi) in reaction 1.

NMR characterization of these complexes were confined to **1a**–**3a** because of the paramagnetic nature of **1b**–**3b** and **1c**–**3c**. ^{13}C NMR spectroscopy proved most useful. Each complex could clearly be distinguished from the starting material **4** (Table I). In addition most complexes could be distinguished from each other. The pattern and multiplicity of absorptions seen was consistent with a pentahapto structure for **1a**–**3a** although a trihapto structure was not rigorously excluded. A rapidly equilibrating monohapto structure which would have been in accord with these spectral data was excluded by the absence of any significant shift on substitution of a CD_3 group for a CH_3 group.[12,13] Solutions of **1a** did not disproportionate over the period of a month at room temperature although **1a** and **3a** did disproportionate to form a mixture of **1a**, **2a**, and **3a**.

Complexes **1**–**3** were also characterized by IR and UV–visible spectroscopy.[14] UV–visible spectra of **1**–**3** had maximum absorptions in the UV region at longer wavelength relative to heptamethylindenyl and were very similar to KHmi in THF.[15] The visible spectra of the Nd and Er complexes exhibited the f–f transitions characteristic of the trivalent state of these lanthanide ions.

Taken together these results show that the heptamethylindenyl ligand does indeed allow the isolation of some previously unavailable types of organolanthanide complexes. Further studies of synthesis of other lanthanide complexes of this ligand and applications of the resulting complexes are continuing.

Acknowledgment. We are grateful to the Robert A. Welch Foundation, a grant-in-aid from the Ministry of Education of Japan, and the Department of Energy for support of this research. Funds for the Varian XL-200 NMR spectrometer used in this work were provided, in part, by a National Science Foundation grant to Texas A&M University (CHE78-03230).

Registry No. 1a, 80434-36-2; **1b**, 80422-17-9; **1c**, 80422-18-0; **2a**, 80422-19-1; **2b**, 80422-20-4; **2c**, 80422-21-5; **3a**, 80422-22-6; **3b**, 80422-23-7; **3c**, 80434-37-3; **4**, 80422-16-8.

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(12) This deuterated ligand, Hmi-d_3 was prepared by a route similar to that previous described[11] by using CD_3Li instead of CH_3Li.

(13) Faller, J. W.; Murray, H. H.; Saunders, M. *J. Am. Chem. Soc.* **1980**, *102*, 2306–2309.

(14) HMI and all of its derivatives show similar infrared absorptions. IR (Nujol mull) 1640 (w) and 1580 (w) (C=C and ring skeletal vibration), 1300 (w or m), 1280 (w), 1160 (m), 1100 (m), 1080 (w), 1050 (w), 1020 (s), and 1000 (s) (ring-methyl in-plane deformation), 970 (w), 920 (w), 840 (w), 770 (w), and 660 (w) (ring–methyl out-of-plane deformation) cm^{-1}. The absorption intensities of the complexes are stronger at 1300 cm^{-1} and weaker at 1640 cm^{-1} than those of Hmi-H, respectively. Some complexes show THF absorptions at 1050 and 900 cm^{-1}.

(15) UV spectra in THF: heptamethylindene, 226 and 267 nm; metal complexes, ca. 230 and 270 nm. Visible spectra (nm) in THF: **3c**, 810, 751, 588*, 530, 515; **2c**, 815, 805, 748, 599*, 535, 520; **1c**, 807, 750, 587*, 530; 3b, 980, 657, 558, 525*, 492, 442; **2b**, 978, 655, 557, 523*, 490, 452; **1b**, 986, 660, 552, 530*, 493, 455. Asterisks indicate hypersensitive transitions.

The Laser vs. the Lamp. A Novel Laser-Induced Adiabatic Reaction and Luminescence of Benzophenone

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The molecular photophysics and photochemistry of benzophenone and its derivatives in fluid organic solvents represent a keystone in the development and history of mechanistic organic photochemistry.[1] Pulsed laser flash spectroscopy[2] has been an important and powerful method for the determination of the dynamics of quenching and reactions of benzophenone triplets. It is generally assumed that the nature and behavior of the photochemistry and photophysics of a system are qualitatively the same whether laser excitation or conventional steady-state lamp excitation is employed. We report here evidence that a laser, but not a conventional lamp, can induce a novel, unprecedented emission from benzophenone and substituted benzophenones.[3]

Excimer laser excitation (15-ns pulse; 249, 308, or 351 nm) of benzophenone in Freon-113 (5×10^{-5}–10^{-2} M) produces the emission spectra[4] shown in Figure 1. At relatively low laser power (curve c, 18 mJ) the observed spectrum is very similar to the phosphorescence produced by conventional lamp excitation of benzophenone. Increasing the laser power (curves a and b) or using a focused beam results in the observation of a new emission whose maximum (after subtraction of the conventional benzophenone phosphorescence)[5] occurs at 520 nm. This novel emission

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(1) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978.

(2) Wolf, M. W.; Legg, K. D.; Brown, R. E.; Singer, L. A.; Parks, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 4490 and references therein.

(3) We are aware of the skepticism and caution that should be applied to the proposal of any novel effects for an intensity studied system. Artifacts can always bedevil such proposals: Lemire, A.; Mar, A.; Maharaj, U.; Dong, D. C.; Cheung, S.-T.; Winnik, M. A. *J. Photochem.* **1980**, *14*, 265.

(4) Emission spectra were recorded on a PAR gateable OMA II system. Transient absorption spectra were monitored with a system that has been described earlier: Turro, N. J.; Aikawa, M.; Butcher, J.; Griffin, G. *J. Am. Chem. Soc.* **1980**, *102*, 5127.

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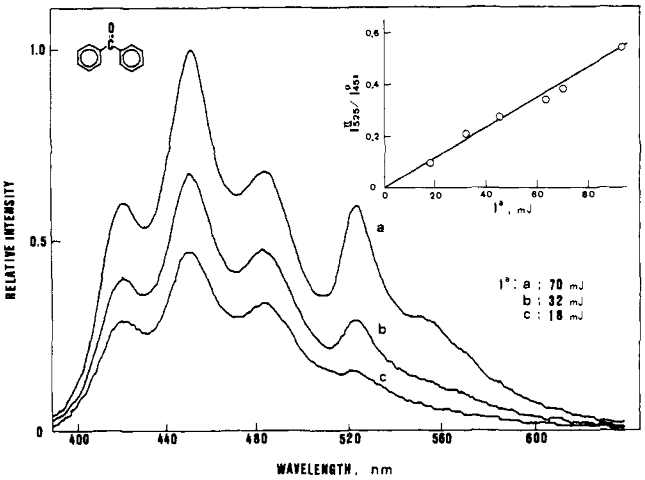

Figure 1. Effects of the exciting light intensity on the emission spectrum of benzophenone (3.0×10^{-3} M) in Freon at room temperature (25 °C). Excitation wavelength 351 nm. Excitation intensity, I^{a}: (a) 70; (b) 32; (c) 18 mJ/pulse. Inset: The plot of emission intensity ratio I_{525}^{11}/I_{451}^{p} against the excitation intensity.

Table I. Pulsed Laser Excitation of Benzophenone and Some Derivative

ketone	phosphorescence λ_{max}, nm	emission of X λ_{max}, nm
benzophenone	451	525
4-methoxybenzophenone	448	no emission
4-methylbenzophenone	450	532
4-chlorobenzophenone	453	539
4-(carbomethoxy)benzophenone	465	556
4,4'-bis(trifluoromethyl)benzophenone	461	532
4,4'-difluorobenzophenone	442	no emission
4,4'-dimethoxybenzophenone	444	no emission

is assigned to an electronically excited transient, X*, since no evidence for irreversible photoreaction could be obtained (UV and VPC analysis) after 100 laser pulses, and the emission is also observed in perfluorinated ether (Freon E-1). Certain substituted benzophenones (Table I) also display a corresponding novel emission in Freon-113 and CCl_4. The time-resolved total emission spectrum (Figure 2) shown for a substituted benzophenone clearly demonstrates that in the time domain of ~1–10 μs, the novel emission increases relative to conventional phosphorescence. After about 20 μs (for laser power of ~85 mJ), the novel emission decays in intensity, relative to conventional phosphorescence. In no case was this novel emission observed in hydrogen-donating solvents (cyclohexane, *n*-propyl alcohol, or toluene) or in inert polar solvents (acetonitrile and *tert*-butyl alcohol).

The ratio of the intensity of the novel emission to the phosphorescence emission is a monotonic function of laser power (inset in Figure 1). The intensity of the novel emission is proportional to the square of the laser excitation power, a result which suggests that production of a photon from X* requires two photons, i.e., the novel emission results from an interaction of two excited ketone molecules.

The decay of benzophenone triplets ($^3BP^*$) was monitored both by time-resolved absorption spectroscopy (λ_{ph}^{obsd} = 525 nm) and by time-resolved phosphorescence spectroscopy (λ_{ph}^{obsd} = 425 nm). By both methods of analysis, triplet decay follows mixed first- and second-order kinetics. However, at higher laser powers the triplet decay rate shows a laser power dependence and obeys clean second-order kinetics for ≳90% of the triplet decay. Furthermore, the buildup time of the novel emission at 520 nm corresponds roughly to 300–400 ns under a given set of conditions and is followed by a decay. The latter decay is power dependent.

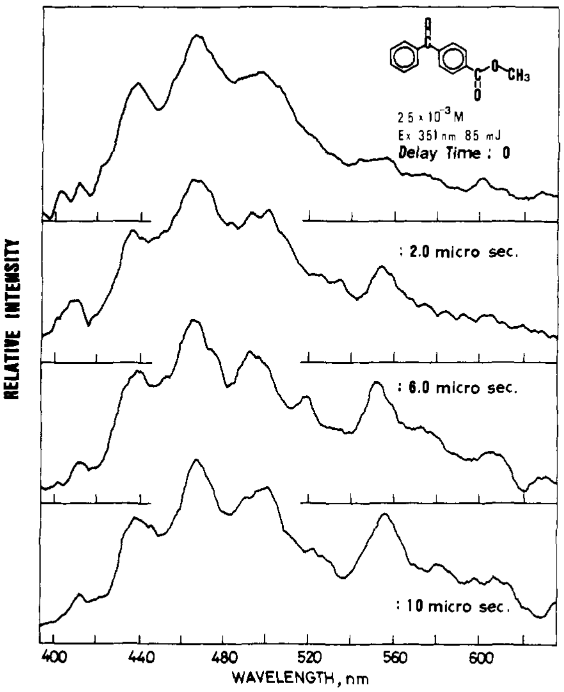

Figure 2. Time-resolved emission spectra of 4-(carbomethoxy)benzophenone (2.5×10^{-3} M) in Freon at room temperature (25 °C). Excitation wavelength 351 nm; excitation intensity 85 mJ/pulse; gate time 2.0 μs. Each spectrum is normalized at 465 nm.

The above results are consistent with the mechanism shown in steps 1–7 where BP = benzophenone (or a substituted benzophenone).

$$BP + h\nu \rightarrow {}^1BP^* \rightarrow {}^3BP^* \tag{1}$$

$${}^3BP^* + {}^3BP^* \rightarrow \text{no } X^* \tag{2}$$

$${}^3BP^* + {}^3BP^* \rightarrow X^* \tag{3}$$

$$X^* \rightarrow X + h\nu_{525} \tag{4}$$

$$X^* \rightarrow \text{no } h\nu_{525} \tag{5}$$

$${}^3BP^* \rightarrow BP + h\nu_{425} \tag{6}$$

$${}^3BP^* \rightarrow \text{no } h\nu_{425} \tag{7}$$

The mechanism is consistent with the salient features of the data: (a) At low laser intensities (≲15 mJ) steps 6 and 7 determine the $^3BP^*$ lifetime; normal phosphorescence (425 nm) is observed from step 6, and the triplet decay is first order. (b) At high laser intensities steps 2 and 3 determine the $^3BP^*$ lifetime; emission from both steps 4 and 6 are observed. (c) In polar "inert" solvents (acetonitrile and *tert*-butyl alcohol) for which the unimolecular decay of $^3BP^*$ is relatively slow, emission from X* would not be observed if step 3 and/or step 4 become insignificant. (d) In nonpolar, hydrogen-donating solvents (isooctane), hydrogen abstraction occurs such that $^3BP^*$ decay is pseudo first order.

The question then arises as to the nature of X*. An electronically excited complex possessing or capable of acquiring charge-transfer (CT) character is one possibility. Indeed, the established pathways for bimolecular quenching of an n,π* state by ground-state molecules suggest that two distinct geometries of approach (perpendicular and parallel) are probable.[6] Fur-

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(5) Among the numerous previous reports of benzophenone phosphorescence in Freons and CCl_4, we are unable to find a mention of this novel emission: Parker, C. A.; Joyce, T. A. *Chem. Commun.* **1968**, 749. *Trans. Faraday Soc.* **1969**, *65*, 2823. Saltiel, J.; Curtis, H. C.; Metts, L.; Miley, J. W.; Winterle, J.; Wrighton, M. *J. Am. Chem. Soc.* **1970**, *92*, 410. Giering, L.; Bergen, M.; Steel, C. *Ibid.* **1974**, *96*, 953.

(6) The concepts here are analogous to those suggested earlier to rationalize the quenching of benzophenone triplets by aromatic solvents and the self-quenching of benzophenones: Schuster, D. I. *Pure Appl. Chem.* **1975**, *41*, 601. Wolf, M. W.; Brown, R. E.; Singler, L. A. *J. Am. Chem. Soc.* **1977**, *99*, 526.

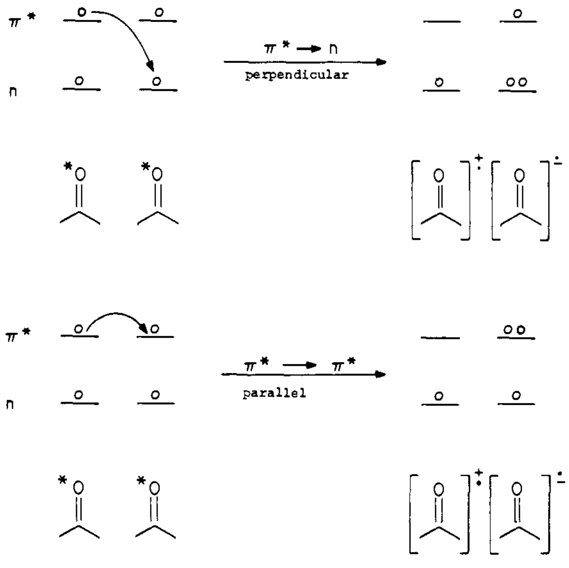

Figure 3. Molecular orbital diagram for the interaction of two n,π* excited states. For simplicity, an extreme CT situation is depicted. The emission of X* could be due either to a local transition perturbed by the companion ketone of the complex or to a transition involving both partners.

thermore, for the n,π* state in either pathway, the n orbital is a potential one-electron acceptor and the π* orbital is a potential one-electron donor. Which of these acceptor-donor properties is manifest depends on the species interacting with the n,π* state. If we postulate[8] that the interactions of *two* n,π* triplets are analogous to those of an n,π* triplet and a ground state, then the simple MO diagram given in Figure 3 suggests that a perpendicular approach should favor a π* → n CT interaction, whereas a parallel approach should favor a π* → π* interaction (in the latter case, the system need not be symmetrical in order to take advantage of CT interactions). For the π* → π* interaction, the model indicates that an electronically excited complex X* is favored. The solvent effects on the emission of X* are expected if it possesses considerable substantial CT character, since radiationless relaxation pathways of such species are known to be strongly favored by increasing solvent polarity.[7b] The absence of emission may be due to several factors including short triplet lifetimes which allow first-order decay to dominate even at high laser powers and to differences in quenching mechanisms, e.g., π* → n interactions (Figure 3) in the triplet-triplet annihilation step.

Although the above proposal is consistent with our observations, several rather ad hoc postulates are required. We, therefore, mention that two other possibilities could be considered to explain the unusual emission, namely, that triplet-triplet interactions produce a structure that is difficult or impossible to achieve via triplet-ground state interactions. For example, two triplets can interact cooperatively to stimulate an emission analogous to the "dimole" emission of excited pairs of oxygen molecules.[9] However, the energy of this emission would be expected to be observed at much higher, not lower, energies than that of a single triplet. A second possibility is that X* is an emissive excimer and that its formation does not occur via triplet-ground state interactions.[10]

In conclusion, at high laser intensities excitation of benzophenone and certain substituted benzophenones in nonpolar, inert solvents results in the observation of a novel emission that is attributed to an electronically excited complex produced by triplet-triplet interactions.

Acknowledgment. We thank the Air Force Office of Scientific Research and the National Science Foundation for their generous support of this research. Professor Larry Singer is also thanked for his kind gift of several of the ketones employed in this study.

Registry No. Benzophenone, 119-61-9; 4-methoxybenzophenone, 611-94-9; 4-methylbenzophenone, 134-84-9; 4-chlorobenzophenone, 134-85-0; 4-(carbomethoxy)benzophenone, 6158-54-9; 4,4′-bis(trifluoromethyl)benzophenone, 21221-91-0; 4,4′-difluorobenzophenone, 345-92-6; 4,4′-dimethoxybenzophenone, 90-96-0.

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(8) Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41.

(9) Kasha, M.; Brabham, D. E. *Org. Chem. (N.Y.)* **1979**, *40*, 1. We thank a referee for this clever suggestion.

(10) Dr. T. Evans of Kodak Co. has suggested that the annihilation of two triplets could lead to the geometry that is required for excimer formation.

(11) Thus, it is conceivable that excimer formation via the "usual" excited-state-ground-state interactions is unfavorable, whereas excimer formation via excited-state-excited-state interaction is favorable.

Metal-Metal Bonded Complexes of the Early Transition Metals. 3. Synthesis, Structure, and Reactivity of $Ta_2Cl_4(PMe_3)_4H_2$ (Ta═Ta)[1]

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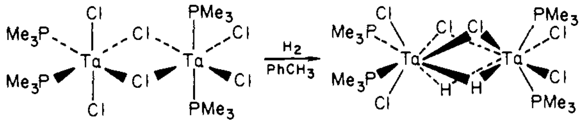
Metal-metal bonded binuclear complexes of the group 5 transition elements are quite rare,[2] especially when compared to the plethora of such compounds in group 6 chemistry.[3] We are currently exploring the binuclear chemistry of the group 5 elements in search of new structural and reactivity patterns. Our initial investigations[2f] led to the synthesis of the tantalum(III) dimer, $Ta_2Cl_6(PMe_3)_4$ (**1**), whose edge-sharing bioctahedral geometry contrasts with the confacial bioctahedral stereochemistry found earlier in the tetrahydrothiophene (THT) complexes of Templeton and McCarley,[2b] e.g., $Ta_2Br_6(THT)_3$. Compound **1** is the only known metal-metal multiply bonded (Ta═Ta) complex which reacts directly (reaction 1) with molecular hydrogen, and it does so under very mild conditions (25 °C, 1 atm of H_2) to form the quadruply bridged tantalum(IV) dimer, $Ta_2Cl_6(PMe_3)_4H_2$ (**2**).[2f] We have now found that **2** offers a convenient entry into tantalum(III) dimer chemistry.



1 **2** (1)

Reduction of **2** in ethylene glycol dimethyl ether (glyme) with 2 equiv of sodium amalgam (reaction 2) provides air-sensitive, deep green, crystalline **3** in essentially quantitative yield.[4]

$$\underset{\mathbf{2}}{\mathrm{Ta_2Cl_6(PMe_3)_4H_2}} + 2\mathrm{Na/Hg} \xrightarrow{(\mathrm{CH_3OCH_2})_2} \underset{\mathbf{3}}{\mathrm{Ta_2Cl_4(PMe_3)_4H_2}} + 2\ \mathrm{NaCl} \quad (2)$$

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(1) Part 2: Sattelberger, A. P.; McLaughlin, K. W.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2880-2882.

(2) (a) Broil, A.; Schnering, H. G.; Schäfer, H. *J. Less-Common Met.* **1970**, *22*, 243-245. (b) Templeton, J. L.; Dorman, W. C.; Clardy, J. C.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 1263-1267. (c) Cotton, F. A.; Millar, M. *J. Am. Chem. Soc.* **1977**, *99*, 7886-7891. (d) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2354-2356. (e) Cotton, F. A.; Najjar, R. C. *Inorg. Chem.* **1981**, *20*, 2716-2719. (f) Sattelberger, A. P.; Wilson, R. B., Jr.; Huffman, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7111-7113.

(3) (a) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; Chapter 26. (b) Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225-232. (c) Chisholm, M. H.; Cotton, F. A. *Ibid.* **1978**, *11*, 356-362. (d) Templeton, J. L. *Prog. Inorg. Chem.* **1979**, *26*, 211-300.

(4) Elemental analyses and molecular weight measurements were performed by Galbraith Laboratories, Knoxville, TN. Anal. Calcd for $Ta_2Cl_4(PMe_3)_4H_2$ ($Ta_2Cl_4P_4C_{12}H_{38}$): C, 17.78; H, 4.69; Cl, 17.51; M_r, 810. Found: C, 17.82; H, 4.65; Cl, 17.84; M_r, 813.

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