

has resulted in a conventional unweighted residual, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, of 0.041. The crystal used for data collection gave slightly more than one-half copper sphere of data before the six standard reflections being monitored every 300 reflections showed a sharp decrease in intensity, presumably due to a rapid degradation of the compound. The remaining intensity measurements necessary for a complete set of θ - 2θ scan data (at least to $2\theta_{\text{MoK}\alpha} = 55^\circ$) will be made on other crystals of this compound and then merged with the present data set. The additional data will be necessary if we are to make the best possible comparisons between the structural parameters of this complex and others in a series containing halogen substituted cyclopentadienyl groups.

$(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5\text{Mn}$ is composed of discrete molecules in which the manganese atom achieves a filled valence shell configuration by bonding octahedrally to five carbonyl groups and a σ -bonded pentachlorocyclopentadienyl ligand (Figure 1). The C_5Cl_5^- group is bonded to the manganese atom through a single carbon atom at a distance of 2.204 (6) Å and possesses the normal characteristics of a σ -bonded cyclopentadienyl group, namely two short, 1.351 (8, 6, 6)⁹ Å, and three long, 1.487 (8, 12, 13) Å, carbon-carbon bonds. The four carbon atoms of the cyclopentadienyl ring involved in the two double bonds are bonded to chlorine atoms at an average distance of 1.693 (6, 4, 5) Å, while the fifth carbon atom is bonded to a chlorine atom at a distance of 1.798 (6) Å—observations also consistent with a σ -bonded cyclopentadienyl ring. The four carbonyl groups, whose carbon atoms form a quasi-square oriented approximately normal to the Mn-CP1 vector, have average manganese-carbon bond lengths of 1.871 (8, 10, 21) Å, while the group trans to the pentachlorocyclopentadienyl group has a manganese-carbon bond of 1.833 (8) Å. The carbonyl groups are bonded linearly to the manganese (average Mn-C-O angle of 177.2 (8, 6, 14)⁹) and have average values of 1.151 (8, 4, 7) Å for the carbon-oxygen distances.

Compound I is stable in the solid state. Samples exposed to light or air show no visible signs of deterioration. It melts, with effervescence, at 110° to give quantitative yields of II. This conversion also takes place slowly in solution at room temperature and may account for the isolation of II from the original reaction mixture.

When II is the sole product desired, the insertion reaction is carried out in octane. After 24 hr at room temperature, the reaction solution is warmed to ~80° for a few minutes, cooled, and stripped to dryness. Sublimation of the residue yields II uncontaminated by I. The infrared spectrum (cyclohexane solution) of II in the carbonyl stretching region shows two bands at 2050 (s) and 1982 (vs) cm^{-1} assigned to the A_1 and E modes, respectively. These are shifted an average of 28 cm^{-1} to higher wave numbers than those observed for $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_5\text{Mn}$. This suggests that the $\eta^5\text{-C}_5\text{Cl}_5$ ring is a poorer electron donor and/or better electron acceptor than the $\eta^5\text{-C}_5\text{H}_5$ moiety. The solid state spectrum of II, excluding carbonyl related vibrations, has fewer bands than that of compound I and is

(9) The first number in parentheses is the rms estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the average value, respectively.

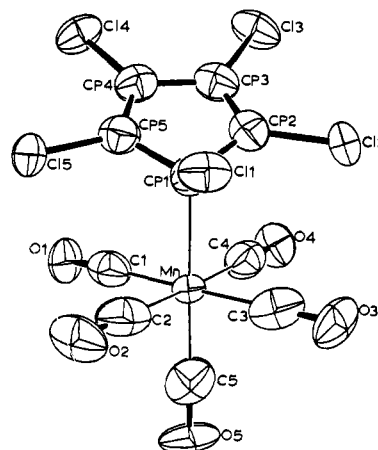


Figure 1. The molecular structure of $(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5\text{Mn}$.

similar to that reported for $\text{Fe}(\text{C}_5\text{Cl}_5)_2$.¹ This is expected for η^5 coordination of the pentachlorocyclopentadienyl group.¹⁰

The relative stability of $(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5\text{Mn}$ is notable, as $(\eta^1\text{-C}_5\text{H}_5)(\text{CO})_5\text{Mn}$ is not known. This may be due to the decreased nucleophilicity of C_5Cl_5^- ¹¹ relative to C_5H_5^- so that displacement of two carbonyl groups is less readily achieved. Also, the well-known ability of halogens to stabilize metal-carbon σ -bonds¹² probably contributes to the stability of I.¹³

Investigation of the chemical properties of these complexes is currently in progress.

Acknowledgment. The advice and interest of Professor H. C. Clark, in whose laboratories the preparative work was conducted, are gratefully acknowledged.

(10) H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 239 (1964).

(11) R. West, *Accounts Chem. Res.*, **3**, 130 (1970).

(12) M. L. H. Green in "Organometallic Compounds," Vol. II., G. E. Coates, M. L. H. Green, and K. Wade, Ed., Methuen, London, 1968.

(13) When $(\eta^5\text{-C}_5\text{H}_5\text{Cl})(\text{CO})_5\text{Mn}$ and $[\eta^5\text{-C}_5(\text{C}_6\text{H}_5)_4\text{Cl}](\text{CO})_5\text{Mn}$ were prepared *via* reaction of the appropriate diazocyclopentadienes, no evidence was found for stable η^1 derivatives.¹⁴ This emphasizes the importance of both factors.

(14) K. J. Reimer, unpublished observations.

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Iodo- and Hydridotantalum(III) Complexes of Dialkylacetylenes

Sir:

The isolation and study of stable transition metal complexes of monoolefins and acetylenes and their derivatives have provided insight into transition metal catalyzed reactions of these hydrocarbons. Heretofore most of these studies have been restricted to systems involving olefins or acetylenes which are activated by electronegative substituents,¹ with relatively few ex-

(1) See, for example, A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, **94**, 1886 (1972); J. Schwartz, D. W. Hart, and J. L. Holden, *ibid.*, **94**, 9269 (1972).

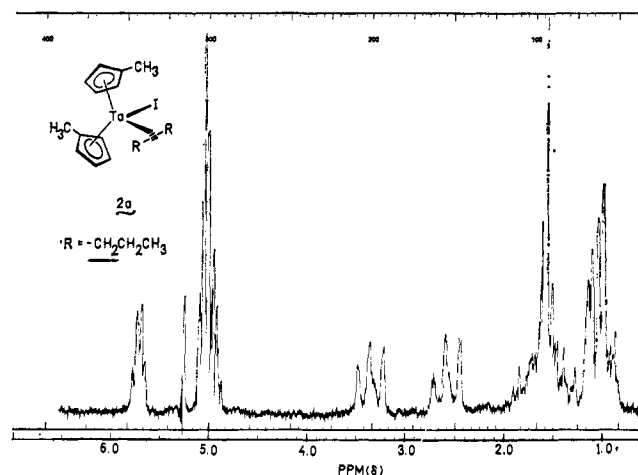


Figure 1. Recorded at 60 MHz in C_6D_6 .

ceptions, stable complexes of unsaturated ligands with alkyl substituents, only, have not been reported. To prepare reactive complexes of "unactivated" unsaturated hydrocarbons (such as dialkylacetylenes) would expand in scope the synthetic and mechanistic studies thus far available only to their activated counterparts. In this context, we wish to report the synthesis of two such classes of compounds.

Complexes of the type $Cp_2MH(C_2H_4)$ ($M = Nb, Ta$; $Cp = \eta^5-C_5H_5$)² possess remarkable stability, and we have been able to prepare hydridotantalum(dialkylacetylene) complexes by direct reaction³ of the hydrocarbon with $(MeCp)_2TaH_3$ ($MeCp = \eta^5-C_5H_4CH_3$)⁴ (1).⁴ These unusual complexes are more readily made in high yield *via* iodotantalum(acetylene) precursors which are easily obtained and purified. We believe that the hydrido(acetylene) complexes described herein are the first isolable examples of their type and may be models for intermediates in insertion reactions of metal hydrides and "unactivated" acetylenes.

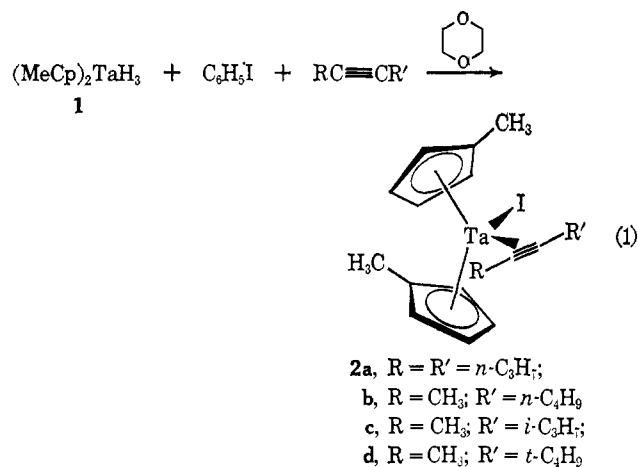
Moderately air-stable, crystalline $(MeCp)_2TaI$ (dialkylacetylene) (2) can be prepared from 1 as follows. In a typical experiment, a solution of 1 (1.1 g, 3.2 mmol), oct-4-yne (720 mg, 6.4 mmol), and iodobenzene (670 mg, 3.2 mmol) in 8 ml of dioxane was heated to reflux under inert atmosphere. Rapid darkening of the reaction mixture occurred. After 10 min, solvent was removed *in vacuo*,⁵ and golden yellow crystals of $(MeCp)_2TaI$ (oct-4-yne) (2a) (870 mg, 47%) were isolated by cooling hexane extracts of the residue. The product was characterized by elemental analysis, ir ($\nu_{CC} = 1775\text{ cm}^{-1}$, in $n-C_6H_{14}$), and 1H nmr. The 1H nmr spectrum of 2a (Figure 1) suggests the structure indicated in reaction 1 in which the $C=C$ bond lies in a plane containing the Ta and I atoms. The resulting nonequivalence of the two halves of the acetylene molecule is clearly indicated.^{6,7} Complexes of the unsymmetrical acetylenes

(2) F. N. Tebbe and G. W. Parshall, *J. Amer. Chem. Soc.*, **93**, 3793 (1971).

(3) Hydrido(acetylene) complexes are slowly formed on refluxing 1 with the acetylene in toluene.

(4) This compound is more readily accessible than the unmethylated analog: U. Klabunde and G. W. Parshall, *J. Amer. Chem. Soc.*, **94**, 9081 (1972).

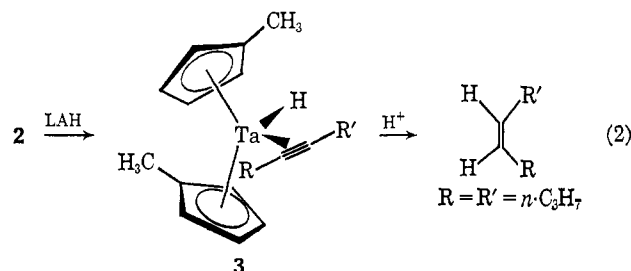
(5) Vpc analysis of the volatiles shows formation of 1 mol of benzene per mol of 1 consumed and consumption of slightly more than 1 mol of oct-4-yne per mol of 3a formed. No oct-4-ene or other hydrogenated C_8 species was found.



hept-2-yne (2b), 4-methylpent-2-yne (2c), and 4,4-dimethylpent-2-yne (2d) were prepared. In each case, the 1H nmr spectrum was similar to that of 2a and showed the presence of two isomers since the acetylene can possess one of two orientations relative to the other ligands.⁸

Refluxing a solution of 2 with excess $LiAlH_4$ in ether smoothly produces hydride complex 3 (for 3a, $\nu_{CC} = 1770\text{ cm}^{-1}$)⁹ (reaction 2). The 60-MHz 1H nmr spectrum of 3a in C_6D_6 shows the nonequivalence of the halves of the octyne ligand (τ_{Ta-H} 10.2, $\tau_{CH_2(R' \text{ or } R)}$ 7.2 (t, $J = 7\text{ Hz}$), $\tau_{CH_2(R' \text{ or } R)}$ = 7.1 (t, $J = 7\text{ Hz}$)). Reaction of 3 with iodobenzene in refluxing dioxane regenerates the iodo complex 2.

Treatment of a solution of 3a at room temperature with HBF_4 causes rapid precipitation of solid and liberation of a nearly quantitative amount of *cis*-oct-4-ene. Formation of *cis* olefin is postulated to occur *via* initial protonation of the metal¹⁰ followed by insertion of the acetylene into the Ta-H bond and C-H reductive elimination (reaction 2). The composition of the precipitate has not yet been determined. Compound 3 also reacts slowly with H_2 at 100° to yield *cis*-oct-4-ene



it has not yet been determined. Compound 3 also reacts slowly with H_2 at 100° to yield *cis*-oct-4-ene

(6) A similar effect was observed in the 1H nmr spectrum of $W(CO)_5(\text{hex-3-yne})$: D. P. Tate, J. M. Augl, W. M. Ritchey, B. L. Ross, and J. G. Grasselli, *J. Amer. Chem. Soc.*, **86**, 3261 (1964).

(7) The barrier to rotation of the coordinated acetylene is apparently quite high; no broadening or coalescence of the signals due to the two kinds of propargylic protons was observed up to 110° , above which decomposition becomes significant.

(8) The ring proton region of the spectrum of all complexes 2 and 3 is considerably more complex than in the parent $(MeCp)_2TaH_3$. This is attributable to the fact that all four protons in each ring become nonequivalent when the plane of symmetry bisecting the rings is lost. This increased complexity can also be seen in comparing the spectra of $(MeCp)_2ZrCl_2$ and $((MeCp)_2ZrCl)_2O$: E. Samuel, *Bull. Soc. Chim. Fr.*, 3548 (1966).

(9) The ir band centered at 1770 cm^{-1} has a shoulder at *ca.* 1800 cm^{-1} which is attributed to Ta-H stretching. In support of this assignment, this peak is shifted to 1275 cm^{-1} for the corresponding deuteride.

(10) Protonation of the isoelectronic complex $Cp_2NbH(PR_3)_2$ to give stable $Cp_2NbH_2(PR_3)_2^+$ has been reported: C. R. Lucas and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1005 (1972).

(reaction 2). We are continuing our investigations of the chemistry of complexes 2 and 3 and are extending our studies to include the potentially more reactive Nb(III) analogs.

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Intramolecular Cation Exchange in [3]Cryptates of Alkaline Earth Cations¹

Sir:

Among the variety of properties displayed by natural and synthetic ligands of alkali and alkaline earth cations,²⁻⁵ a specially fascinating one resides in their ability to promote cation transport through natural or artificial membranes, either as carriers⁶ or by forming trans-membrane channels.⁷ Very little is known about such cation propagation along a chain of binding sites at the molecular level. We present here a study of cation jumping rates between binding sites inside the cavity of a synthetic molecule.

The macrotricyclic ligand, L, forms 1/1 inclusion complexes of the [3]cryptate type with various monovalent and bivalent cations.⁸ The stability constants of the alkaline earth cation complexes have now been determined by pH-metric titration; $\log K_s = 6.53, 6.97,$ and 8.0 for $\text{Ca}^{2+}, \text{Sr}^{2+},$ and Ba^{2+} cations, respectively (aqueous solutions of L + metal chloride salts). These bivalent [3]cryptates $[\text{M}^{2+} \subset \text{L}]^9$ display an intramolecular cation exchange process which may be studied by ^{13}C nmr spectroscopy.¹⁰

The ^{13}C Fourier transform nmr spectrum of L in D_2O displays four singlets with relative areas 1:2:1:2 corresponding respectively to the $\text{C}_\text{B}-\text{O}, \text{C}_\text{R}-\text{O}, \text{C}_\text{B}-\text{N},$ and $\text{C}_\text{R}-\text{N}$ carbon atoms.¹¹

On addition of *alkali cation* salts the four ^{13}C signals shift smoothly and level off at high cation/L molar ratios, indicating the progressive formation of weak $[\text{M}^+ \subset \text{L}]$ complexes⁸ with fast cation exchange.

When increasing amounts of salts of *alkaline earth*

(1) Cryptates. XIII. Part XII: B. Dietrich and J. M. Lehn, *Tetrahedron Lett.*, 1225 (1973).

(2) R. J. P. Williams, *Quart. Rev., Chem. Soc.*, 24, 331 (1970).

(3) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, 11, 16 (1972).

(4) C. H. Hassall and W. A. Thomas, *Chem. Brit.*, 7, 145 (1971).

(5) J. M. Lehn, *Struct. Bonding (Berlin)*, 16, 1 (1973).

(6) P. Lauser, *Angew. Chem.*, 81, 56 (1969); B. C. Pressman, *Ann. N. Y. Acad. Sci.*, 147, 829 (1969); H. K. Wipf, A. Olivier, and W. Simon, *Helv. Chim. Acta*, 53, 1605 (1970); R. Ashton and L. K. Steinrauf, *J. Mol. Biol.*, 49, 547 (1970); M. Kirch and J. M. Lehn, to be submitted for publication.

(7) D. W. Urry, *Proc. Nat. Acad. Sci. U. S.*, 68, 672 (1972); 69, 1610 (1972), and references therein.

(8) J. Cheney, J. M. Lehn, J. P. Sauvage, and M. E. Stubbs, *J. Chem. Soc., Chem. Commun.*, 1100 (1972).

(9) The mathematical sign of inclusion $\text{A} \subset \text{B}$ (B includes A) is used to specifically designate inclusion complexes.⁵

(10) The spectra have been measured on a Varian XL-100/15 spectrometer in the Fourier transform mode at 25.14 MHz with noise decoupling of the protons.

(11) The R and B subscripts designate respectively carbon atoms in the 12-membered rings and in the two bridges linking the two rings.

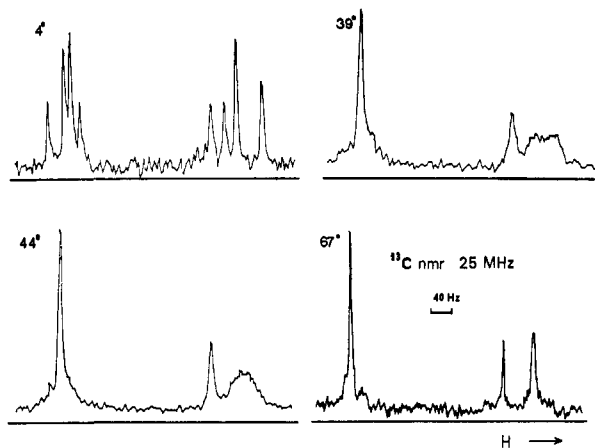


Figure 1. ^{13}C FT nmr spectra of the $[\text{Ca}^{2+} \subset \text{L}]_2\text{Cl}^-$ complex at different temperatures (D_2O solution of L + excess CaCl_2). At 4° , the chemical shifts are: 23.3, 25.2 ($\text{C}_\text{R}-\text{N}$); 26.1, 27.2 ($\text{C}_\text{B}-\text{N}$); 37.2, 39.6 ($\text{C}_\text{B}-\text{O}$); 37.9, 38.5 ($\text{C}_\text{R}-\text{O}$) ppm (downfield from CH_3 of internal *tert*-butyl alcohol).

cations ($\text{CaCl}_2, \text{SrCl}_2, \text{BaCl}_2$) are added to a D_2O solution of L, new ^{13}C lines appear, which grow while the signals of the free ligand decrease to zero as one reaches a 1/1 stoichiometry. No further changes occur on addition of more salt. The new spectra are those of the bivalent [3]cryptates $[\text{M}^{2+} \subset \text{L}]$ and are temperature dependent (see Table I).

Table I. Spectral Parameters, Coalescence Temperatures, Exchange Rates, and Free Energies of Activation for Intramolecular Cation Exchange in $[\text{M}^{2+} \subset \text{L}]_2\text{Cl}^-$ Cryptates^{10, 11, a}

Compound	^{13}C signal	$\Delta\nu, \pm 2$ Hz (temp, $^\circ\text{C}$)	$T_c,$ $\pm 4^\circ\text{C}$	$k_c,$ sec^{-1}	$\Delta G_c^\ddagger,$ ± 0.3 kcal/mol
$[\text{Ca}^{2+} \subset \text{L}]_2\text{Cl}^-$	$\text{C}_\text{R}-\text{N}$	48 (4)	40	107	15.4
	$\text{C}_\text{B}-\text{N}$	26 (4)	30	58	15.3
	$\text{C}_\text{R}-\text{N}^b$	21 (32)	~ 105	~ 47	~ 19.5
$[\text{Sr}^{2+} \subset \text{L}]_2\text{Cl}^-$	$\text{C}_\text{R}-\text{N}$	77 (5)	27	171	14.5
	$\text{C}_\text{B}-\text{N}$	26 (5)	15	58	14.5
$[\text{Ba}^{2+} \subset \text{L}]_2\text{Cl}^-$	$\text{C}_\text{R}-\text{N}$	70°	< 3	> 155	< 13.3
$[\text{La}^{3+} \subset \text{L}]_3\text{NO}_3^-$	$\text{C}_\text{R}-\text{N}$	26 (32)	> 93	< 58	> 18.6

^a $\Delta\nu$, separation of the ^{13}C signals at temperature indicated; T_c , coalescence temperature; k_c , exchange rate at coalescence; ΔG_c^\ddagger , free energy of activation at coalescence calculated from T_c and k_c using the Eyring rate equation. The $^{13}\text{C}-\text{O}$ data lead to the same results. The solutions were ca. 150–200 mM L in D_2O . ^b Parameters for the intermolecular exchange process. In the case of $\text{Sr}^{2+}, \text{Ba}^{2+},$ and La^{3+} all coalescences lie well above 100° since all signals are still sharp at this temperature; thus for these cations $\Delta G_c^\ddagger(\text{inter}) > 19$ kcal/mol. ^c Assumed value by analogy with the Sr^{2+} complex.

At $+4^\circ$ two sets of four ^{13}C resonances are observed for the $[\text{Ca}^{2+} \subset \text{L}]$ complex ($\text{C}-\text{O}$ set at low field, $\text{C}-\text{N}$ set at high field, Figure 1). Within each set two signals ($\text{C}_\text{R}-\text{O}, \text{C}_\text{R}-\text{N}$ carbons) have twice the intensity of the other two ($\text{C}_\text{B}-\text{O}, \text{C}_\text{B}-\text{N}$ carbons). When the temperature is raised, the signals of same intensity within each set coalesce and a four-line spectrum (in fact only three lines since the $\text{C}_\text{R}-\text{O}$ and $\text{C}_\text{B}-\text{O}$ lines overlap) is obtained at higher temperatures. Similar results are obtained for the Sr^{2+} complex but the coalescences take place at lower temperatures than with Ca^{2+} . In the case of Ba^{2+} only marked broadening of the upfield $^{13}\text{C}_\text{R}-\text{N}$ signal is observed before freezing out the