Table III. Binding Energies (BE) for Cl (2p) and La (3d) Photoelectron Lines[a, b]

compd	BE		
	La (3d)	Cl ($2p_{1/2}$)	Cl ($2p_{3/2}$)
$LaCl_3$	835.0	197.6	197.0
[Cp(CH$_2$)$_3$Cp]LaCl	833.0	198.8	197.6
Cp$_3$La	831.0	NO[c]	NO[c]

[a] All values in electronvolts (eV). [b] Binding energy scale was chosen for C_{1s} peak–284.8 eV. [c] Not observed.

case of cerium complexes, isotropic shifts are minimal,[19] but the absorption peaks were too broad to be meaningful. For lanthanum complexes the signals at δ 7.57 and 7.74 have a relative integrated intensity of 8 and are assigned to the protons of the Cp groups. The broad peaks at δ 4.24 and 4.54 integrate to 6 and are due to the methylene protons. For the lanthanum phenylethynyl complex the signal at δ 8.92, which integrates to 5, is assigned to phenyl protons.

In the mass spectrum of [Cp(CH$_2$)$_3$Cp]CeCl, the parent ion is only 0.6% as abundant as the most prominent peak at *m/e* 91, and the cerium isotopes are not abundant in the spectrum either. The peak at *m/e* 72 may be formed from the chlorine isotopes or as a residue of the ligand. The lowest intensity peaks were not displaced in the computer output because of the normalization procedure. The most probable fragmentation path appears to be the breaking of the cerium–cyclopentadienyl bonds and the bridge carbon bonds, resulting in seven carbon membered ions (*m/e* 91 and 92). The remaining fragments of this complex at *m/e* 77–80 also appears in the spectrum. Another fragmentation pattern at *m/e* 171, 172, and 173 appears to be the splitting of the Ce-Cl group. Further degradation is indicated by mass peaks at intervals of 14 mass units, indicating the loss of CH$_2$ groups.

The X-ray photoelectron spectra (ESCA) of LaCl$_3$, [Cp(CH$_2$)$_3$Cp]LaCl, and Cp$_3$La were measured. Cl 2p and La 3d photoelectron lines of these three compounds are summarized in Table III. The binding energies of both the Cl $2p_{1/2}$ and Cl $2p_{3/2}$ photopeaks increase slightly as the number of chlorine ions in the molecule are reduced from 3 in LaCl$_3$ to 1 in [Cp(CH$_2$)$_3$Cp]LaCl. The 0.6-eV increase in binding energy of the Cl $2p_{3/2}$ photopeak in [Cp(CH$_2$)$_3$Cp]LaCl relative to LaCl$_3$ is miniscule but important and could be interpreted as a very small decrease in the electronic charge density located in chlorine ions in going from LaCl$_3$ to [Cp(CH$_2$)$_3$Cp]LaCl. In the case of La $3d_{5/2}$ signals, strong satellite peaks were observed on both sides of the parent peaks which, in general, has been the subject of long debate.[20] These satellites which occur at a 3–6 eV higher energy region than that of main peaks have been attributed to charge-transfer shake-up from occupied orbital(s) (L → "4f")[21] If the L → "4f" transition causes the satellite peak, the intensity would be reduced as the number of "f" electrons is constantly increased. This is supported by the observation that the satellite lines of any lanthanum complex are much more intense than in any of the rest of the 14 lanthanide elements. In fact, it is not even observed following cerium in the lanthanide series of the periodic table.

The configuration of these complexes as monomeric or polymeric is still unresolved. Because of their low solubilities the molecular weights have not yet been determined, even though, when freshly prepared, solubilities of these complexes seem to be better. This can be seen; when first synthesized, these complexes are monomeric but slowly changing after a period of time. So that this question may be settled, the complete structure elucidation will shortly be done by X-ray diffraction analysis.

There seems to be no doubt that big anionic ligands can greatly stabilize lanthanides toward σ-bond formation. Here it appears both electronic properties and steric rigidity are operating together. These newly synthesized complexes bridge a gap of the missing dicyclopentadienyl derivatives of the early lanthanides, which in turn eventually will be used for the synthesis of a series of σ-bonded complexes for all the lanthanide elements.

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Registry No. [Cp(CH$_2$)$_3$Cp]LaCl, 75857-12-4; [Cp(CH$_2$)$_3$Cp]LaC≡CPh, 75861-71-1; [Cp(CH$_2$)$_3$Cp]CeCl, 75861-70-0; [Cp(CH$_2$)$_3$Cp]CeC≡CPh, 75861-72-2; LaCl$_3$, 10099-58-8; Cp$_3$La, 1272-23-7.

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Chemistry of the μ_2-Alkyne Ligand in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{RC}{\equiv}\text{CR})$

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An understanding of the chemistry of bridging alkyne ligands in polynuclear metal complexes is important to the overall development of organocluster chemistry. In recent years, we have studied the chemistry of bridging μ_x ($x \geq 2$) alkyne ligands in dinuclear[1,2] and polynuclear[3,4] metal complexes with special emphasis on three types of reactions: (i) alkyne exchange between free and bound alkyne to gain a measure of alkyne–M$_x$ bond strengths and of dynamic features of these complexes; (ii) hydrogen addition reactions to assess alkyne reduction tendencies and also the tendency of the polynuclear complex to fragment into smaller species; (iii) catalytic hydrogenation of alkynes (selectivity). Described below is such a study of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\mu_2\text{-}\eta^2\text{-RC}{\equiv}\text{CR})$ complexes.

Experimental Section

Reagents and Procedures. Solvents were dried by refluxing over sodium and distillation prior to use. Diphenylacetylene purchased from Aldrich Chemical Co. was used without any purification. Di-*p*-tolylacetylene,[5-7] (C$_5$H$_5$)$_2$Ni$_2$(C$_6$H$_5$C$_2$C$_6$H$_5$),[8] (C$_5$H$_5$)$_2$Ni$_2$(C$_7$H$_7$C$_2$C$_7$H$_7$),[8] and (CH$_3$C$_5$H$_4$)$_2$Ni$_2$(C$_6$H$_5$C$_2$C$_6$H$_5$)[8] were prepared by literature procedures.

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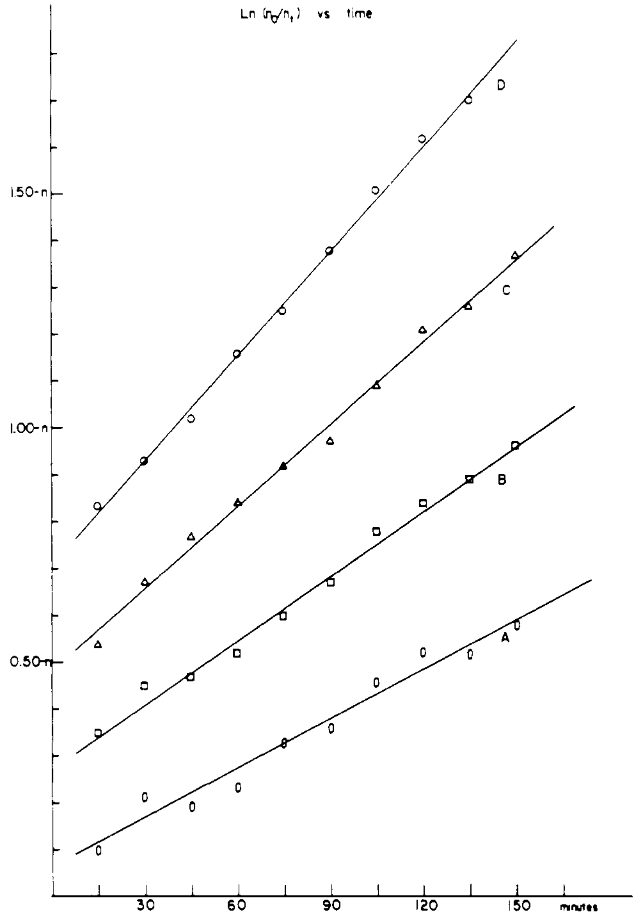

Figure 1. Kinetic analysis of the acetylene-exchange reaction between diphenylacetylene and $(\eta^5\text{-}C_5H_5)_2Ni_2(p\text{-}CH_3C_6H_4C_2\text{-}p\text{-}CH_3C_6H_4)$. The plots show a linear dependence in dimer concentration with time for a fixed concentration of free acetylene. Plots A–D represent respectively ratios of 1:20, 1:30, 1:40, and 1:60 for the molar ratios of $(C_5H_5)_2Ni_2(CH_3C_6H_4C_2C_6H_4CH_3)$ to diphenylacetylene at zero time, t_0. The ordinate has a sliding scale with n = 1, 0.2, 0.4, and 0.6 for plots A–D, respectively. Plotted is ln (n_0/n_t) vs. time (min), with n_0 and n_t the concentrations of $(C_5H_5)_2Ni_2(CH_3C_6H_4C_2C_6H_4CH_3)$ at times t_0 and t, respectively.

All manipulations were performed in an argon atmosphere in a Vacuum Atmospheres Dri-box with a Model HE Dri-Train, with a glass vacuum system or a modified Schlenk system.

Ligand Exchange. Experiments with $(C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$ established the minimal temperature (inlet temperature) and ionizing voltage for detection of the parent ion to be ~90 °C and 50 eV. Analysis of a physical mixture of $(C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$ and $(CH_3C_5H_4)_2Ni_2(C_6H_5C_2C_6H_5)$ under these conditions showed the parent ions for the two complexes and also a substantial one for $(CH_3C_5H_4)(C_5H_5)Ni_2(C_6H_5C_2C_6H_5)$.

Hydrogenation of $(\eta^5\text{-}C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$. A solution of $(\eta^5\text{-}C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$ (0.338 g, 795 × 10^{-5} mol) in 25 mL of mesitylene was placed in a reaction tube. The tube was cooled to −196 °C, evacuated, and filled to a pressure of 1 atm with hydrogen. The tube was then placed in a heating bath at 150 °C for 1.75 h. After this period of time, a film of nickel plate was present. The reaction was repeated at 120 °C for 1.5 h, and again, a film of nickel metal formed. The remaining solution was green, indicating the presence of $(\eta^5\text{-}C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$.

$(C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$ (0.0325 g, 7.37 × 10^{-5} mol) and 3-hexyne (2.5 mL, 2.2 × 10^{-2} mol) were dissolved in 20 mL of mesitylene and placed in a reaction vessel. The tube and contents were cooled to −196 °C, and the tube was evacuated and then filled with hydrogen to a pressure of 1 atm. The tube and contents were allowed to warm to room temperature. The tube was then placed in a heating bath at 150 °C for 12 h. At the end of this time period, a film of nickel metal was present. The reaction was repeated at 140 °C with the same results. At 120 °C, the reaction mixture showed no sign of nickel metal formation. The volatile products were transferred and analyzed by gas chromatography. Analysis showed that no acetylene hydrogenation had occurred. Analysis of the residue by proton nuclear magnetic resonance spectroscopy showed the residue to be a mixture of $(\eta^5\text{-}C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$ and $(\eta^5\text{-}C_5H_5)_2Ni_2(C_2H_5C_2C_2H_5)$.

Table I. Kinetic Analysis: Fit of Rate Data to Interchange for Rate = $(k_1 + k_2[RC_2R])$[Complex]

mol of $[(\eta^5\text{-}C_5H_5)_2\text{-}Ni_2(RC_2R)]$	mol of diphenylacetylene	slope	correlation	intercept
3.44 × 10^{-5}	6.595 × 10^{-4}	3.52 × 10^{-3}	0.985	6.16 × 10^{-2}
3.22 × 10^{-5}	9.978 × 10^{-4}	4.55 × 10^{-3}	0.996	7.71 × 10^{-2}
3.24 × 10^{-5}	1.348 × 10^{-3}	5.89 × 10^{-3}	0.997	7.76 × 10^{-2}
3.308 × 10^{-5}	2.002 × 10^{-3}	7.51 × 10^{-3}	0.999	1.047 × 10^{-1}

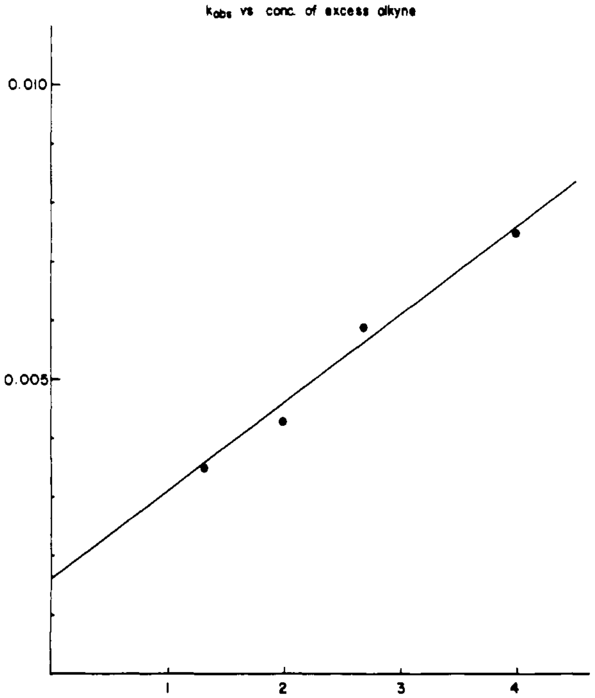

Figure 2. Kinetic analysis of the actylene-exchange reaction illustrating the dependence of rate (L mol^{-1} min^{-1}) on the free acetylene concentration (mol L^{-1}).

Acetylene-Exchange Reaction. A flask containing a solution of $(C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$ (0.0290 g, 6.82 × 10^{-5} mol) and 3-hexyne (0.16 mL, 1.41 × 10^{-3} mol) in 20 mL of mesitylene was placed in a heating bath at 150 °C for 3.5 h. The volatile products were removed after this time by vacuum transfer. The residue was analyzed by ^1H NMR spectroscopy. Analysis showed the residue to be a mixture of $(\eta^5\text{-}C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$ and $(\eta^5\text{-}C_5H_5)_2Ni_2(C_2H_5C_2C_2H_5)$.

For determination of the molecularity of the exchange reaction, a kinetic analysis of the reaction was undertaken. Weighed amounts of $(\eta^5\text{-}C_5H_5)_2Ni_2(CH_3C_6H_4C_2C_6H_4CH_3)$ (~0.015 g, 3.53 × 10^{-5} mol) and diphenylacetylene were dissolved in 0.5 mL of p-xylene. The resulting solutions were heated at 120 °C for 3 h. At 15-min intervals, the tubes were removed from the heating bath. The contents of the tubes were analyzed by ^1H NMR spectroscopy. The relative amounts of $(\eta^5\text{-}C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$ and $(\eta^5\text{-}C_5H_5)_2Ni_2(CH_3C_6H_4C_2C_6H_4CH_3)$ were determined by integration. The linear plots shown in Figure 1 were generated by least-squares analyses of the data (see Table I). A fitting of these data to the interchange rate expression is shown in Figure 2 where the correlation coefficient was 0.996. For the kinetic data obtained at low acetylene:complex ratios, there was a slight variance from the overall interchange rate expression because the back-reaction became significant. A full listing of kinetic data is given in Table II (supplementary material).

$(\eta^5\text{-}C_5H_5)_2Ni_2(p\text{-}CH_3C_6H_4C_2C_6H_4\text{-}p\text{-}CH_3)$ (0.015 g, 3.53 × 10^{-5} mol) was dissolved in 0.5 mL of solvent (a mixture of p-xylene-d_{10} and 1% tetramethylsilane). So that the presence of paramagnetic species *at high temperatures* could be checked, the solution was placed in an NMR tube. Also placed in the NMR tube was a sealed capillary tube containing p-xylene-d_{10} and 1% tetramethylsilane. The NMR tube was sealed under an argon atmosphere. The tube was then heated at 120 °C for 3 h, during which time the solution was monitored by NMR spectroscopy. The above experiment was repeated with use of solutions that contained $(\eta^5\text{-}C_5H_5)_2Ni_2(p\text{-}CH_3C_6H_4C_2C_6H_4\text{-}p\text{-}CH_3)$ and weighed amounts of diphenylacetylene (0.0627 g, 3.52×10^{-4} mol and 0.1255 g, 7.05×10^{-4} mol). The NMR tubes were placed in the NMR probe at 120 °C, and the ^1H NMR spectrum was monitored as a function of time (1–3 h); specifically line width changes and a separation of tetramethylsilane signals (capillary and solution) were sought.

Results and Discussion

Hydrogen did not react with $(C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$ until temperatures slightly above 120 °C were reached at which point hydrogenation and gross decomposition occurred to give a nickel film on the walls of the reaction tube. With mixtures of 3-hexyne and hydrogen, there was no evidence of alkyne hydrogenation catalyzed by the dinuclear nickel acetylene complex at 120 °C, a temperature at which hydrogenative decomposition of the dinuclear complex was not detected. Alkyne exchange occurred at measurable rates between diphenylacetylene and $(C_5H_5)_2Ni_2(p\text{-}CH_3C_6H_4C_2\text{-}p\text{-}CH_3C_6H_4)$ at 120–150 °C. The alkyne-exchange reaction appeared to proceed through mononuclear reaction intermediates; see discussion below. Failure of the dimer to function as a catalyst for alkyne hydrogenation may be ascribed to coordination saturation in the dimeric nickel complex and to thermal reactivity of mononuclear fragments like C_5H_5NiH (possible precursor to nickel metal) resulting from the hydrogen reaction above 120 °C.

Alkyne exchange between free alkyne and the dinuclear metal alkyne complex could be rationalized by a number of plausible mechanisms. One pathway would be fragmentation to mononuclear complexes (eq 1) either through an associative

$$(C_5H_5)_2Ni_2(RC_2R) + R'C_2R' \rightleftharpoons C_5H_5Ni(RC_2R) + C_5H_5Ni(R'C_2R') \quad (1)$$

first step or through a dissociative set of reactions involving a first step of dissociation into C_5H_5Ni and $C_5H_5Ni(RC_2R)$ fragments. We attempted to establish whether fragmentation was occurring in these exchange reactions by using a mixture of ring-labeled dimers, $(C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$ and $(CH_3C_5H_4)_2Ni_2(C_6H_5C_2C_6H_5)$. Scrambling occurred to give substantial amounts of $(C_5H_5)(CH_3C_5H_4)Ni_2(C_6H_5C_2C_6H_5)$ simply on mass spectrometric analysis of physical mixtures of the C_5H_5 and $CH_3C_5H_4$ dimers (mass spectrometer inlet at 90 °C). Thus, the alkyne-exchange reaction could not be monitored because of the extensive scrambling that occurred in the mass spectrometric analysis. However, the very fact that scrambling occurred so readily under relatively mild (thermal) conditions in the mass spectrometer suggests that alkyne exchange by fragmentation a la eq 1 is a reasonable reaction course. Also, it has been shown that $Co_2(CO)_8$ reacts with $(C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$ at 70 °C to form substantial quantities (25% isolated yield) of $(C_5H_5)NiCo(CO)_3(\mu_2\text{-}C_6H_5C_2C_6H_5)$.[9]

The molecularity of the acetylene-exchange reaction in xylene solution was examined, and a rate expression of the form rate = $(k_1 + k_2[RC_2R])$[complex] (see Figures 1 and 2) was obtained with values for k_1 and k_2 of 1.62×10^{-3} min^{-1} and 1.5×10^{-3} L mol^{-1} min^{-1}, respectively. These data alone are mechanistically nondefinitive; the rate expression has the ubiquitous interchange form for reactions of transition-metal complexes. Collectively, however, the kinetic and chemical reactivity data are *suggestive* of a fragmentation pathway with the key intermediate a 17-electron species, $C_5H_5Ni(RC_2R)$. Competitive with this pathway would be interchange with the generation of $C_5H_5Ni(RC_2R)$ and $C_5H_5Ni(\eta^x\text{-}p\text{-xylene})$ species. Nevertheless, the alternative interchange sequence $[(C_5H_5)_2Ni_2(RC_2R)] + S\ (\text{solvent}) \rightleftharpoons [(C_5H_5)_2Ni_2S] + RC_2R$ cannot be excluded by our data. This alkyne-exchange reaction for the nickel dinuclear complex differs qualitatively from that based on $(C_5H_5)_2Mo_2(CO)_4(RC_2R)$ where fragmentation does not occur[1] and the initial, rate-determining step in exchange comprises dissociation of a CO ligand.

The suggested mononuclear intermediates for the acetylene-exchange mechanism would be paramagnetic. Attempts by NMR spectroscopy to detect such a species at 120 °C over several hour periods were unsuccessful for solutions of $(\eta^5\text{-}C_5H_5)_2Ni_2(p\text{-}CH_3C_6H_4C_2C_6H_4\text{-}p\text{-}CH_3)$ and for solutions of this complex with 1 and 10 equiv of excess diphenylacetylene.[10] Clearly, such fragments, if they were responsible for the acetylene exchange process, must be present in low concentration at 120 °C, a feature not inconsistent with the relatively low rate of acetylene exchange in the reaction systems.

Acknowledgment. This research was supported by a grant from the National Science Foundation.

Registry No. $(\eta^5\text{-}C_5H_5)_2Ni_2(C_6H_5C_2C_6H_5)$, 35828-66-1; $(\eta^5\text{-}C_5H_5)_2Ni_2(C_2H_5C_2C_2H_5)$, 76096-33-8; $(\eta^5\text{-}C_5H_5)_2Ni_2(CH_3C_6H_4C_2C_6H_4CH_3)$, 76529-88-9; $C_6H_5C_2C_6H_5$, 501-65-5.

Supplementary Material Available: A listing of kinetic data for the acetylene exchange reaction (1 page). Ordering information is given on any current masthead page.

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(10) Solutions of the acetylene complex in perdeuterioxylene with 1% tetramethylsilane as a reference with a capillary containing 1% tetramethylsilane in deuterioxylene were sealed in an NMR tube. This tube was placed in the spectrometer probe heated to 120 °C. There was no significant shift in the resonances at these temperatures and no significant line broadening. The same observations were made for solutions of the complex with added diphenylacetylene.

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Crystal and Molecular Structure of a Substitution-Labile Chromium(III) Complex: Aquo(ethylenediaminetriacetatoacetic acid)chromium(III)

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Chromium(III) octahedral complexes are generally inert to the substitution of inner-sphere water molecules by other ligands. Recent reports indicate, however, the chromium(III) complexed with one water molecule and a five-coordinate EDTA-type ligand shows unexpectedly rapid substitution rates with several anionic ligands.[1,2] It has been suggested that these reaction rates are due in part to strains present in the complex.[3] The crystal and molecular structure determination of $[Cr(H_2O)HEDTA]$ has been undertaken to ascertain the extent of distortion from octahedral geometry that is present in the molecule in the solid state. The crystal structure of $[Cr(H_2O)HEDTA]$ has previously been shown to be isomorphous to the structure reported for Fe(III),[4] Ga(III),[4] and Rh(III)[5] complexes.

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