2226 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2226—2230 (1971) [Vol. 44, No. 8

Electronic Spectra of Square-Planar Bis(tertiary phosphine)dialkynyl Complexes of Nickel(II), Palladium(II), and Platinum(II)

Haruo Masai, Kenkichi Sonogashira, and Nobue Hagihara
The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka

(Received February 27, 1971)

Electronic spectra of *trans*-[$L_2M(C\equiv CR)_2$], (L=tertiary phosphine or tertiary stibine, and M=Ni, Pd or Pt) have been studied in solution from 220 mμ to 360 mμ. Nickel and platinum complexes showed three intense absorption bands. The lowest energy band was particularly sensitive to substituents of alkynyl groups. This band was assigned empirically to the transition between the molecular orbitals involved in metal-alkynyl bonds. The possibility of π-interaction between the two alkynyl groups through central metal was discussed in relation to the influence of R.

We have been studying the properties of bis(tertiary phosphine)dialkynyl complexes, *trans*-[$L_2M(C\equiv CR)_2$], where L is a tertiary phosphine or tertiary stibine, and M is nickel(II), palladium(II), and platinum (II). In a previous paper,[1] infrared spectra of the series of the complexes were discussed. From the influence of substituent R upon metal-carbon stretching frequencies, *dπ–pπ* interaction (back-donation) was regarded as an important factor which reinforces the metal-alkynyl bond. The result threw light upon properties of the metal-carbon σ-bond which plays an important role in many reactions catalyzed by transition metal complexes.

For a discussion of the properties of this series of complexes, information on their electronic structure is necessary. However, only a few discussions on the electronic spectra of alkynyl complexes or of complexes having D_{2h} symmetry can be found.[2,3] Theoretical treatment of the spectra of these metals has been limited to the complexes in D_{4h} or T_d symmetry.

In this work, electronic spectra (220 mμ—360 mμ) of the series of alkynyl complexes in solution are reported and their general trends discussed in terms of π-interaction between metal and alkynyl groups.

Results and Discussion

General Features. Electronic spectra (UV) of *trans*-[$L_2M(C\equiv CR)_2$], where M is Ni (II), Pd (II) or Pt (II), and L is a tertiary phosphine or stibine, were recorded in ether from 220 mμ to 360 mμ. Their absorption maxima (λ_{max}) and intensities (log ε) are listed in Table 1.

The intensities of absorption band are of the order of 4 in log ε scale. Thus, these bands are presumably due to the allowed transition within the molecule, *i.e.* intramolecular charge-transfer transition.[4] In our case, no band due to *d-d* transition was observed. It is probably obscured by intense charge-transfer bands.

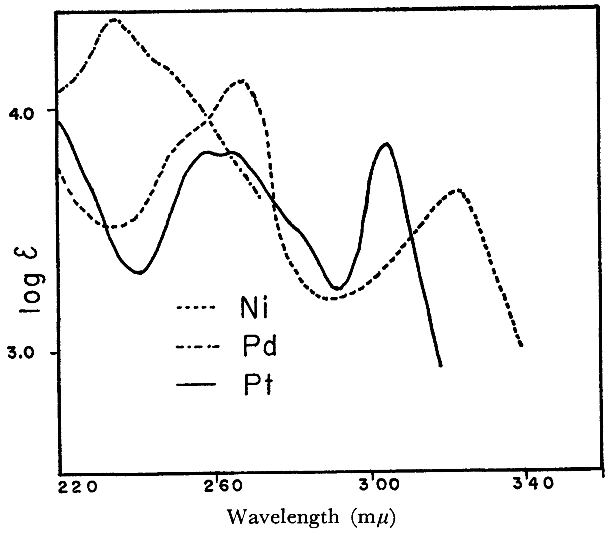

Fig. 1. Electronic spectra of *trans*-[$(Et_3P)_2M(C\equiv CH)_2$] in ether.

The complexes show three intense absorption bands in this region expect for palladium complexes (Fig. 1 and Table 1), which exhibit unresolved bands at the shorter wavelength region than the others. Thus, we mainly discussed nickel and platinum complexes.

The characteristic feature of the palladium complexes has also been observed in UV spectra of teracyanide complexes of nickel(II), palladium(II) and platinum (II).[5,6]

Influence of Substituents of Alkynyl Groups. The change in substituents R's influences the wavelength of three absorption bands in different degrees (Fig. 2). The lowest energy band is most remarkably influenced as shown in Fig.2 and Table 1. Influence on the other bands was not clear, since in some cases they overlapped each other.

It is seen from Table 1 that the lowest energy band is subject to bathochromic effect of the substituents which increases in the following order.

$$R=H<CH_3<CH_2F<CH_2{=}CH<HC\equiv C<Ph<CH_3C\equiv C$$

for *trans*-[$(Et_3P)_2Ni(C\equiv CR)_2$]

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[1] H. Masai, K. Sonogashira, and N. Hagihara, *J. Organometal. Chem.*, **26**, 271 (1971).

[2] P. J. Kim, H. Masai, K. Sonogashira, and N. Hagihara, *Inorg. Nucl. Chem. Lett.*, **6**, 181 (1970).

[3] J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, **1958**, 486.

[4] B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York (1966), Chapter 9.

[5] a) H. B. Gray and C. J. Ballhausen, *J. Amer. Chem. Soc.*, **85**, 260 (1963). b) W. R. Mason, III, and H. B. Gray, *ibid.*, **90**, 5721 (1968).

[6] A. J. McCaffery, P. N. Schatz, and P. J. Stephans, *ibid.*, **90**, 5730 (1968).

TABLE 1. ABSORPTION BANDS (mμ) AND INTENSITIES (log ε) OF *trans*-$[L_2M(C\equiv CR)_2]$ IN ETHER

M	L	R	λ_{max} (log ε)		
Ni	Et_3P	H	322 (3.68)	266 (4.14)	254sh (3.93)
		CH_3	329 (3.68)	272 (3.87)	260sh (3.67)
		CH_2F	315br (3.74)	271 (4.16)	260sh (3.97)
		$CH_2{=}CH$	338 (3.15)	269 (3.51)	256sh (3.45)
		$HC\equiv C$[a]	341 (4.28)		
		Ph	343 (4.01)	275 (4.34)	
		$CH_3C\equiv C$[a]	343 (4.12)		
Pd	Et_3P	H	263sh (3.85)	245sh (4.16)	234 (4.37)
		CH_3	265sh (3.85)	251sh (4.09)	236 (4.32)
		Ph	300sh (4.46)	280sh (4.49)	245 (4.59)
Pt	Et_3P	H	304 (3.85)	267 (3.81)	258 (3.83)
		CH_3	313 (3.95)	276 (3.72)	258 (3.77)
		$CH_2{=}CH$	323 (4.24)	286 (4.01)	260 (4.38)
		$HC\equiv C$	321 (4.01)		
		$CH_3C\equiv C$[a]	324 (4.12)		
		Ph	328 (4.22)	288 (4.13)	264 (4.23)
		$PhC\equiv C$	349 (4.67)		
	Me_3P	H	302 (3.90)	265sh (3.90)	254 (3.93)
		CH_3	310 (4.21)	274sh (4.04)	255 (4.12)
		$CH_2{=}CH$	319 (4.35)	284 (4.13)	258 (4.47)
		Ph	325 (4.47)	285 (4.38)	261 (4.48)
	Et_3Sb	Ph	354 (4.37)	268 (4.77)	242 (4.62)
		$PhC\equiv C$	364 (4.59)		

a) see also Table 4. sh: shoulder

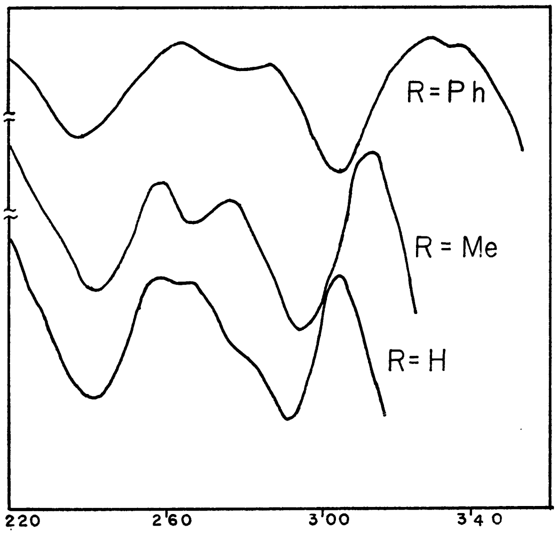

Fig. 2. Influence of R on spectra of *trans*-$[(Et_3P)_2Pt(C\equiv CR)_2]$ in ether.

$R{=}H<CH_3<HC\equiv C<CH_2{=}CH<CH_3C\equiv C<Ph<PhC\equiv C$

for *trans*-$[(Et_3P)_2Pt(C\equiv CR)_2]$ and

$R{=}H<CH_3<CH_2{=}CH<Ph$

for *trans*-$[(Me_3P)_2Pt(C\equiv CR)_2]$

Complicated absorption bands of butadiynyl derivatives (Fig. 3)may be assigned by a solvent effect. Plots of the position of the lowest energy band against ionization potentials (IP) of free alkynes[7] showed a linear correlation (Table 2 and Fig. 4).

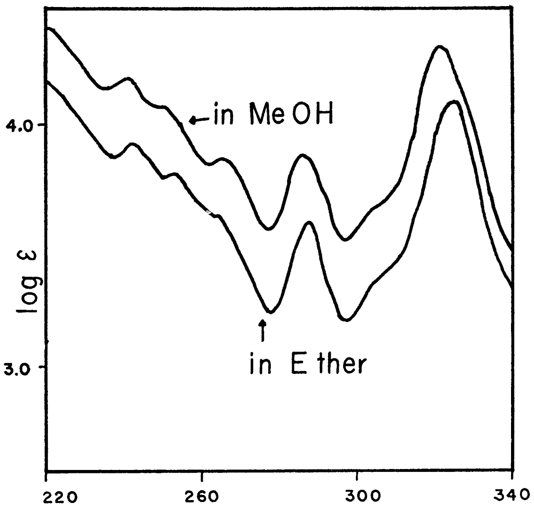

Fig. 3. Electronic spectra of *trans*-$[(Et_3P)_2Pt(C\equiv CC\equiv CCH_3)_2]$ in ether and methanol.

The lowest band is evidently due to the charge-transfer transition involved in metal-carbon bonds as deduced from the remarkable influence of alkynyl groups. The relative one-electron energy diagram for these complexes (D_{2h} symmetry) is shown in Fig.

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[7] V. I. Vedenyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," Edward Arnold, London (1966), Table 8.

Table 2. Energy of lowest bands in eV scale (a), and IP's of free alkynes (b)

(a) *trans*-[$L_2M(C{\equiv}CR)_2$]

M	L	R=H	CH_3	CH_2=CH	HC≡C	Ph
Ni	Et_3P	3.84	3.76	3.66	3.63	3.60
Pt	Et_3P	4.07	3.96	3.83	3.86	3.77
	Me_3P	4.10	3.99	3.88		3.81

(b) IP's of RC≡CH (eV)

R=H	CH_3	CH_2=CH	HC≡C	Ph
11.40	10.36	9.9	10.2	9.15

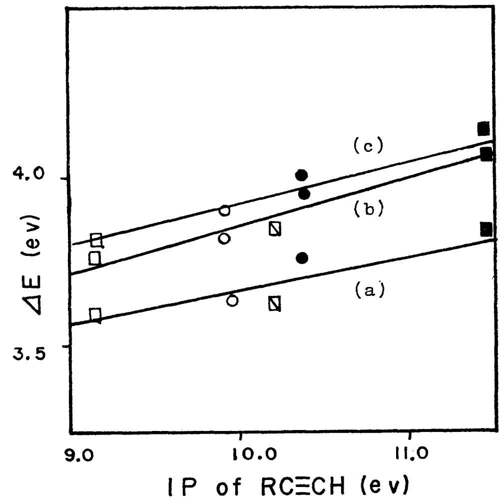

Fig. 4. Plots of transition energy of lowest bands (ΔE) against ionization potentials (IP) of RC≡CH; ■ R=H, ● R=CH_3, ▨ R=HC≡C, ○ R=CH_2=CH, □ R=Ph.
(a) *trans*-[$(Et_3P)_2Ni(C{\equiv}CR)_2$] (b) *trans*-[$(Et_3P)_2Pt(C{\equiv}CR)_2$] (c) *trans*-[$(Me_3P)_2Pt(C{\equiv}CR)_2$]

Table 3. Orbital transformation scheme for *trans*-[$L_2M(C{\equiv}CR)_2$], (D_{2h})

Representation	Metal orbital	Ligand orbital	Remark
A_g	$d_{z^2}, d_{x^2-y^2}$	$\sqrt{1/2}(\sigma_1+\sigma_3)$	C≡CR
	s	$\sqrt{1/2}(\sigma_2+\sigma_4)$	L
B_{1g}	d_{xy}	$\sqrt{1/2}(\pi_{1h}+\pi_{3h})$	C≡CR
		$\sqrt{1/2}(\pi_{2h}+\pi_{4h})$	L
B_{2g}	d_{xz}	$\sqrt{1/2}(\pi_{2v}+\pi_{4v})$	L
B_{3g}	d_{yz}	$\sqrt{1/2}(\pi_{1v}+\pi_{3v})$	C≡CR
B_{1u}	p_z	$\sqrt{1/2}(\pi_{1v}-\pi_{2v})$	C≡CR
		$\sqrt{1/2}(\pi_{4v}-\pi_{2v})$	L
B_{2u}	p_y	$\sqrt{1/2}(\sigma_1-\sigma_3)$	C≡CR
		$\sqrt{1/2}(\pi_{4h}-\pi_{2h})$	L
B_{3u}	p_x	$\sqrt{1/2}(\sigma_2-\sigma_4)$	L
		$\sqrt{1/2}(\pi_{1h}-\pi_{3h})$	C≡CR

6, and the orbital transformation scheme in Table 3, derived from diagrams of tetracyanide complexes[5,6,8] and from our simple molecular orbital calculation.[9] The coordinate system is shown in Fig. 5.

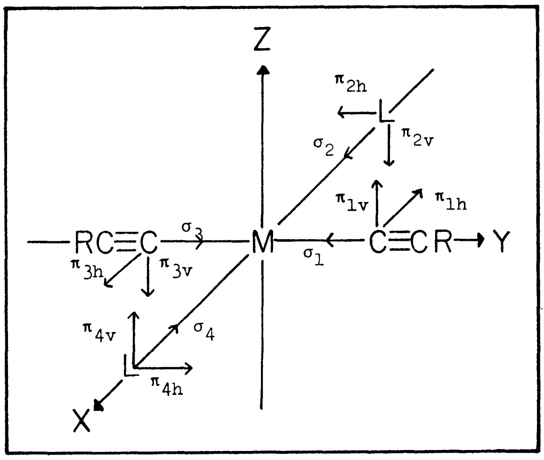

Fig. 5. Coordination system for the complex, *trans*-[L_2M-($C{\equiv}CR)_2$].

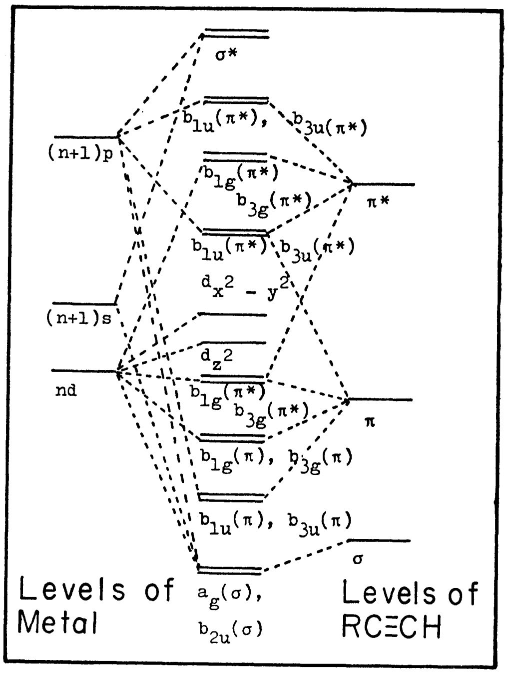

Fig. 6. Relative energy diagram of metal-carbon bond in *trans*-[$L_2M(C{\equiv}CR)_2$].

The correlation shown in Fig. 4 suggests that the lowest band is presumably due to the transition from molecular orbitals consisting of bonding π-orbitals of alkynyl groups, *i.e.* $b_{1g}(\pi)$, or $b_{3g}(\pi)$, to $b_{3u}(\pi^*)$ or $b_{1u}(\pi^*)$ which contains the metal p-orbitals (Fig. 6 and Table 3).

The order of bathochromic shift of substituents is quite different from that of the square of metal-carbon stretching frequencies observed in the infrared spectra,[1] because the former concerns both ground and excited states and the latter only properties of the ground state.

The order of the bathochromic effect of R's is consistent with the increasing order of electronegativity

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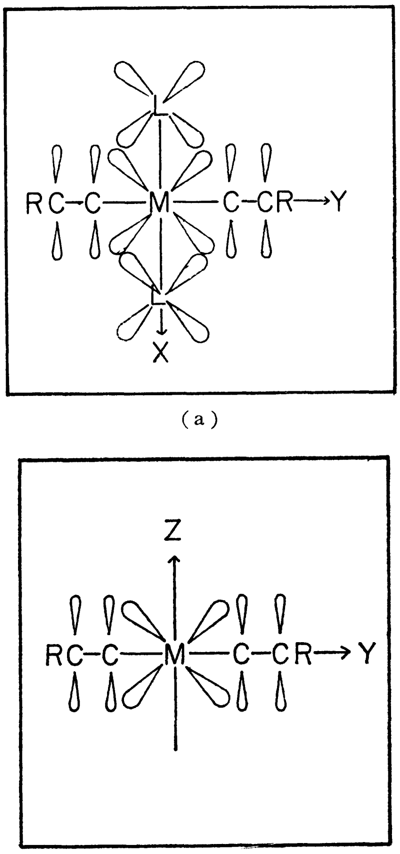
[8] S. Kida, J. Fujita, K. Nakamoto, and R. Tsuchida, This Bulletin, **31**, 79 (1958).

[9] N. Takeuchi, private communication.

of R's induced by the mesomeric effect, though some deviation was observed in nickel complexes.

As shown in Fig. 7, two alkynyl groups can mutually interact through metal d_{xy} and d_{yz} orbitals. Hence, a long conjugate system involving the metal d-orbitals is formed in the *trans* square-planar dialkynyl complexes, and b_{1g} (π) and b_{3g} (π) orbitals are used for the interaction. The bathochromic shift of the lowest band is regarded as evidence for existence of the conjugate system.



(a)

(b)

Fig. 7. Interaction between metal *d*-orbitals and alkynyl π-orbitals;
(a) *X*-*Y* plane (b) *Y*-*Z* plane

Table 4. Influence of solvents

(a) *trans*-$[(Et_3P)_2Ni(C{\equiv}CCH_3)_2]$

Solvent	Absorption band (mμ)		
n-hexane	329	272	260 sh
CH_2Cl_2	330	274	252 sh
CH_3CN	329	272	260 sh
C_6H_{12}	330	272	261 sh
MeOH	326	272	260 sh
EtOH	326	272	260 sh
i-PrOH	327	272	260 sh

sh; shoulder C_6H_{12}; cyclohexane

(b) *trans*-$[(Et_3P)_2Pt(C{\equiv}CCH_3)_2]$

Solvent	Absorption band (mμ)		
CH_2Cl_2	313	277	259
C_6H_{12}	314	277	258
ether	313	276	258
MeOH	308	274	257
i-PrOH	309	274	257

C_6H_{12}; cyclohexane

(c) *trans*-$[(Me_3P)_2Pt(C{\equiv}CH)_2]$

Solvent	Absorption band (mμ)		
C_6H_{12}	303	266	254
ether	302	265 sh	254
MeOH	299	265 sh	254
EtOH	299	262 sh	254
i-PrOH	300	262 sh	254

sh; shoulder C_6H_{12}; cyclohexane

(d) *trans*-$[(Et_3P_2)_2Ni(C{\equiv}CC{\equiv}CH)_2)_2]$

Solvent	Absorption band (mμ)			
ether	341	279 sh	268	252
MeOH	340	278 sh	268	252

sh; shoulder

(e) *trans*-$[(Et_3P)_2Ni(C{\equiv}CC{\equiv}CCH_3)_2]$

Solvent	Absorption band (mμ)			
ether	343	283	267	251
MeOH	342	282	267	251

(f) *trans*-$[(Et_3P)_2Pt(C{\equiv}CC{\equiv}CCH_3)_2]$

Solvent	Absorption band (mμ)					
ether	324	307 sh	287	266 sh	253	243
MeOH	322	305 sh	287	267	252	241

sh; shoulder

Influence of Solvents. Since the solution spectrum is inevitably influenced by solvents, we have studied the influence on the spectra of alkynyl complexes. There was no systematic influence on the intensities of absorption maxima. However, the lowest bands of the spectra showed a blue shift in alcohols (Fig. 8 and Table 4). No appreciable influence was observed in other solvents, such as *n*-hexane, cyclohexane, dichloromethane and acetonitrile, *i.e.* neither polar nor *n*-donor properties of solvents had influence upon the spectra.

The specific influence of alcohols is regarded as a consequence of some interaction between OH group and the alkynyl complexes. Formation of hydrogen bonding may be responsible for this effect. Here, proton acceptor orbitals are considered to be b_{3g} orbitals from the result of a study on electron donor-acceptor complexes.[10)]

Butadiynyl derivatives, *trans*-$[(Et_3P)_2M(C{\equiv}CC{\equiv}CR)_2]$, (M = Ni or Pt, R = H, CH_3 or Ph), gave very complicated spectra (Fig. 3). However, the lowest bands of these spectra displayed a similar behavior to those of the other alkynyl complexes in alcoholic solvents (Table 4 and Fig. 3). Thus, these bands may be regarded as the same as the lowest

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[10)] H. Masai, K. Sonogashira, and N. Hagihara, *J. Organometal. Chem.*, in press.

Table 5. Novel alkynyl complexes, *trans*-[$L_2M(C\equiv CR)_2$]

M	L	R	Found C(%)	Found H(%)	Calcd C(%)	Calcd H(%)	mp (°C)
Ni	Et_3P	$CH_3C\equiv C$	63.00	8.81	62.74	8.62	121—122[a]
Pd	Et_3P	H	49.19	8.46	48.93	8.22	53— 56
		CH_3	51.21	8.44	51.37	8.62	85— 86
Pt	Et_3P	$CH_3C\equiv C$	47.59	6.70	47.39	6.51	156—157
	Me_3P	H	30.22	5.36	30.23	5.07	120[b]
		CH_3	34.04	6.16	33.88	5.69	105[b]

a) melted with decomposition
b) decomposed above this temperature

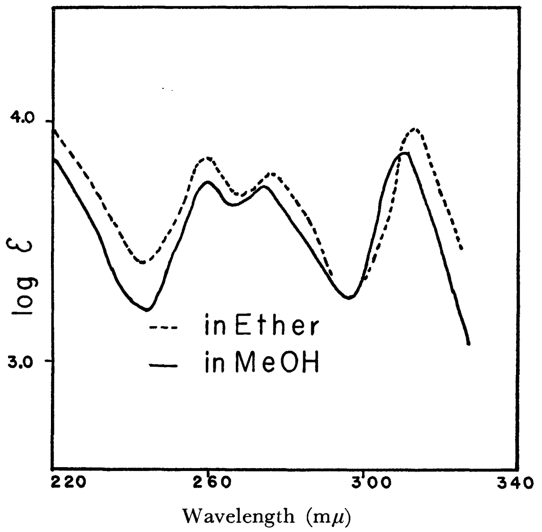

Fig. 8. Influence of solvents on spectra of *trans*-[$(Et_3P)_2Pt(C\equiv CCH_3)_2$].

energy bands of the other alkynyl complexes.

Experimental

Electronic Spectra. Electronic spectra were recorded by a Hitachi EPS-3T recording spectrophotometer using 10 mm quartz cell.

Materials. *(a) Pentadiynyl Complexes,* trans-[$(Et_3P)_2M(C\equiv CC\equiv CCH_3)_2$], *(M = Ni or Pt)*: These complexes were prepared from the reaction of [$(Et_3P)_2MCl_2$] with $CH_3C\equiv CC\equiv CNa$ in liquid ammonia which were prepared in situ from the reaction of $CH_3CCl_2CH_2CCl_2CH_3$ with 5 fold excess of sodium amide (Table 5).

(b) Other Complexes: Other complexes listed in Table 5 were prepared by the same procedure as described previously.[1]

The authors are grateful to Dr. Akira Nakamura, Osaka University, and Dr. Nozomu Takeuchi, Tokushima University, for their helpful discussions.