Journal of Organometallic Chemistry, 108 (1976) 225—233

PREPARATION AND INFRARED SPECTRA OF MONOSUBSTITUTED PR_3 AND $P(OR)_3$ (R = ALKYL, ARYL) DERIVATIVES OF $(\mu_2\text{-L})_2Co_2(CO)_6$ COMPOUNDS *

GYULA VÁRADI **, ANNA VIZI-OROSZ, SÁNDOR VASTAG and GYULA PÁLYI ***

Research Group for Petrochemistry of the Hungarian Academy of Sciences, H-8200 Veszprém (Hungary)

(Received October 7th, 1975)

Summary

$(\mu_2\text{-L})_2Co_2(CO)_5PR_3$ and $(\mu_2\text{-L})_2Co_2(CO)_5P(OR)_3$ (R = alkyl, aryl, $L_2 = P_2$, As_2, acetylene, L = CO and but-2-en-4-olid-4-ylidene) compounds were prepared. The ν(C—O) infrared spectra are in agreement with the expected C_S or C_1 symmetry. The results indicate that the PR_3 or $P(OR)_3$ substituent is in all cases in the axial position.

Introduction

The characterization of $(\mu_2\text{-E}_2)Co_2(CO)_6$ (E = P, As) compounds through their mono-PPh_3 substituted derivatives (I) [2,3,14], as well as recent studies [4] concerning "lactone" complexes [5] $Co_2(CO)_7(C_4O_2RR')$ directed our attention to the series $(\mu_2\text{-L})_2Co_2(CO)_6$.

Literature data on the preparation and/or spectroscopic investigation of $(\mu_2\text{-acetylene})Co_2(CO)_5(PR_3)$ compounds (II) are rare [6—8], while $(\mu_2\text{-but-2-en-4-olide})(\mu_2\text{-CO})Co_2(CO)_5(PR_3)$ complexes (III) have not yet been reported. These compounds seem to be clear cases of C_s or C_1 symmetry, so the number of ν(C—O) bands can be expected to be 5. However, literature data are contradictory in this point.

---

* Some of the results of this work have been presented at symposia [1].

** Present address: Semmelweis University for Medical Sciences, Institute for Biochemistry, Budapest.

*** To whom correspondence should be addressed.

TABLE 1

IR DATA OF $L_2Co(CO)_5PR_3$ COMPOUNDS

Ligands		ν(C—O) values (cm^{-1})					
L_2	PR_3	ν_1	ν_2	ν_3	ν_4	ν_5	$\Delta\bar{\nu}$
P_2	PPh_3	2072.4s	2027.1vs	2020.5s	2006.8w	1984.2m	28.6
P_2	PPh_2Et	2072.6s	2025.4vs	2021.4s	2005.2w	1972.7m	32.2
P_2	P-n-Bu_3	2071.7s	2024.1vs	2018.9s	2002.6m	1978.2m	32.7
As_2	PPh_3	2066.7s	2021.9vs	2016.3s	1999.6w	1978.4m	27.5
As_2	PPh_2Et	2067.4s	2019.1vs(br)		1998.6w	1976.6m	27.9
As_2	$PPhEt_2$	2067.6s	2018.9vs(br)		1998.4m	1976.3m	28.2
As_2	P-n-Bu_3	2065.8s	2019.1vs	2014.5s	1996.2w	1974.0m	30.2
As_2	$P(OEt)_3$	2069.6s	2023.2vs	2016.3vs	2002.8w	1984.6m	24.8

Results and discussion

Preparative results

Compounds I and II were prepared in moderate to good yields (Tables 1 and 2) essentially according to published [2,3,6] procedures in n-hexane, n-hexane/benzene (1 : 1) or benzene as solvent at 20—60°C by treating $E_2Co_2(CO)_6$ and $(R'C_2R'')Co_2(CO)_6$ compounds with 10—25 mole % excess of PR_3. The progress of the reaction was followed by IR spectroscopy and for this reason n-hexane was preferred as solvent where possible. The reaction mixture was chromatographed on silica gel whereby unreacted starting compounds, I or II and 5—20% amounts of disubstituted [6,7], products * could be separated using n-hexane or benzene eluent.

Compounds of type III were prepared similarly (cf. Table 3 and Experimental), but in chromatography n-hexane/ether (1 : 1) had to be used as eluent.

Our experiments were not aimed at collecting systematic data on preparative methods and yields but from the experience accumulated in course of this work it is clear that:

(i) increase in the electron donor character of both the phosphine and the bridging ligand makes substitution more difficult (for example, the PBu_3 derivative of $(Me_3SiC_2Me_3Si)Co_2(CO)_6$ could not be prepared at all and yields of the phosphite derivatives in series III were always higher than those of the PBu_3 derivatives),

(ii) steric factors are also of significance, since the preparation of the P(cyclo-$C_6H_{11})_3$ derivatives was always much more difficult and proceeded with lower yields than that of the PBu_3 analogues.

Efforts to prepare compounds III from derivatives II under milder conditions (50—70 atm CO, 30°C, 2—5 h, high pressure IR cell) than are necessary [5] for the preparation of $Co_2(CO)_7$ $(R'R''C_4O_2)$ complexes have been unsuccesful.

The isomeric composition of compounds I, II and III was tested by repeated elution chromatography. The chromatographically-separated monosubstituted compounds were repeatedly eluted from silica gel or partially (2.5 ×) acetylated cellulose. Narrow cuts were taken which were investigated by IR spectroscopy. No change of the relative intensities and of the shape of bands could be observed

(continued on p. 229)

---

* Full characterization of the behaviour and isomeric composition of these compounds is in progress.

TABLE 2

IR AND PREPARATIVE DATA OF (μ_2-R$'$C$_2$R$''$)Co(CO)$_5$(PR$_3$) COMPOUNDS

Substituents			ν(C—O) values (cm^{-1})						Reaction conditions		
R$'$	R$''$	PR$_3$	ν_1	ν_2	ν_3	ν_4	ν_5	$\Delta\bar{\nu}$	Temperature (°C)	Time (h)	Yield (%)
H	H	P-n-Bu$_3$	2065.5s	2010.0vs	2004.9s	1992.1w	1963.0m(br)	34.6	60	2	30
H	H	P(cyclo-C$_6$H$_{11}$)$_3$	2068.7s	2008.2vs(sh)	2005.0vs(sh)	1990.4w	1963.2m	34.6	60	2	80
H	H	PEt$_2$Ph	2067.5s	2012.0vs(sh)	2007.0vs	1993.0m	1969.9m	31.8	20	12	80
H	H	PEtPh$_2$	2067.6s	2013.3vs	2007.8s	1994.0m	1969.0m	31.4	20	24	80
H	H	PPh$_3$	2068.2s	2016.5s	2008.5vs	1996.8m	1973.9m	28.9	60	2.5	70
H	H	P(O-n-Bu)$_3$	2071.2s	2018.8s	2009.3vs	1997.8m	1976.9w	26.9	60	2	25
H	H	P(OPh)$_3$	2076.8s	2028.2s	2016.3vs	2004.6m	1987.0w	19.1	60	2	30
H	H	AsEt$_3$	2061.5s	2010.4vs	2004.3s	1990.7w	1962.0m	35.9	60	5	20
H	n-Pr	PPh$_3$	2063.0s	2008.4vs	2001.5vs	1988.5m	1965.1m	30.2	60	2.5	40
H	n-Pr	P(OPh)$_3$	2070.6s	2022.3s	2010.9vs	1999.7m	1984.6w	17.9	60	2.5	30
H	n-C$_6$H$_{13}$	P-n-Bu$_3$	2060.0s	2002.3vs		1984.5m	1961.3m	33.1	60	6	50
H	n-C$_6$H$_{13}$	P(cyclo-C$_6$H$_{11}$)$_3$	2058.9s	2000.8vs		1983.4m	1957.0m	33.2	60	4	50
H	n-C$_6$H$_{13}$	PEt$_2$Ph	2061.2s	2003.0vs		1986.8m	1962.4m	31.9	40	2	90
H	n-C$_6$H$_{13}$	PEtPh$_2$	2061.7s	2005.4vs(sh)	2003.4vs(sh)	1988.1w	1963.8m	30.7	40	2	90
H	n-C$_6$H$_{13}$	PPh$_3$	2062.2s	2008.3vs	2002.9vs	1989.6m	1966.3m	29.3	60	2.5	50
H	n-C$_6$H$_{13}$	P(O-n-Bu)$_3$	2065.5s	2012.6s	2004.3vs	1990.8m	1971.4m	26.3	60	2.5	40
H	n-C$_6$H$_{13}$	P(OPh)$_3$	2070.4s	2022.5s	2010.8vs	1996.7m	1988.8w	17.4	60	2.5	80
H	Ph	PPh$_3$	2064.2s	2015.6vs	2005.2vs	1995.8m	1971.8m	29.4	60	2.5	70
Ph	Ph	P-n-Bu$_3$	2060.4s	2010.0vs	2001.9s	1989.5w	1962.6m	32.0	60	2.5	50
Ph	Ph	PPh$_3$	2063.2vs	2017.2s	2005.6s	1995.6m	1972.3w	26.1	60	2.5	30
Ph	Ph	AsEt$_3$	2061.8s	2010.5vs	2004.2s	1991.2m	1962.5m	30.5	60	5	10
SiMe$_3$	SiMe$_3$	P(cyclo-C$_6$H$_{11}$)$_3$	2055.9s	2014.9vs	2004.0s	1996.5m	1974.6m	18.8	60	50	15
SiMe$_3$	SiMe$_3$	P(CH$_2$Ph)$_3$	2056.2vs	2013.2vs	2003.9s	1997.7vs	1966.1m	20.7	60	5	20

TABLE 3

IR DATA OF $Co_2(CO)_6(C_4O_2R', R'')(PR_3)$ COMPOUNDS

Substituents			ν(C—O) values (cm^{-1})										Reaction conditions		
R′	R″	PR_3	ν_1	ν_2	ν_3	ν_4	ν_5	$\Delta\overline{\nu}_t$	ν(bridge)	$\Delta\nu$ (bridge)	ν (organic)	$\Delta\nu$ (organic)	Temperature (°C)	Time (h)	Yield (%)
H	H	P-n-Bu_3	2080,6s	2037.3vs	2029.5s	2012.4s	2000.7ms	32.5	1814.9m	33.4	1775,0	9.8	50	2,5	30
H	H	$P(OPh)_3$	2093.2s	2056.0vs	2044.9s	2028.3s	2020,1m	16.1	1832.3m	16.0	1777.4	7.4	50	2,5	80
H	Me	P-n-Bu_3	2078.1s	2034.7vs	2027.2s	2010.3s	1998.0m	32.5	1814.0m	32.5	1759.8	-	50	2,5	40
H	Me	$P(OPh)_3$	2091.4s	2053.8vs	2042.5s	2026.1s	2016.2m	16.2	1830.4m	16.1	1762.5	-	50	2,5	50
H	n-Pr	P-n-Bu_3	2078.2s	2034.3vs	2026.3s	2009.7s	1996.0m	32.3	1814.2m	32.1	1773.0 1758.1	-	50	2,5	40
H	n-Pr	$P(OPh)_3$	2091.0s	2053.2vs	2042.0s	2025.2s	2017.5mw	16.2	1832.2m	14.0	1776.0 1761.6	-	50	2,5	60
H	Ph	P-n-Bu_3	2080.0s	2036.4vs	2028.7s	2011.5s	2000.1m	31.8	1814.9m	32.2	1759.9	14.0	50	2,5	50
H	Ph	$P(OPh)_3$	2091.9s	2055.5vs	2044.5s	2028.4s	2019.8m	15.1	1830.2m	16.9	1765.2	8.7	50	2,5	70

in the different cuts. This indicates that, at least under the conditions used by us, only one isomer is formed.

Spectra and structure

The ν(C—O) IR spectra are summarized in Tables 1—3. Some characteristic spectra are shown in Fig. 1. It can be seem from the results that in all but five cases the ν(C—O) spectra contain 5 fundamentals, in accordance with the selection rules of C_s ($\Gamma = 3a' + 2a''$) or C_1 ($\Gamma = 5a$) symmetries.

We suggest that the four-band spectra of the exceptions is a result of an apparent "degeneration" of the bands labelled with ν_2 and ν_3. This is in accordance with the broad form and the increased relative intensity of the $\nu_2 + \nu_3$ band with respect to the spectra of other compounds. It should be mentioned

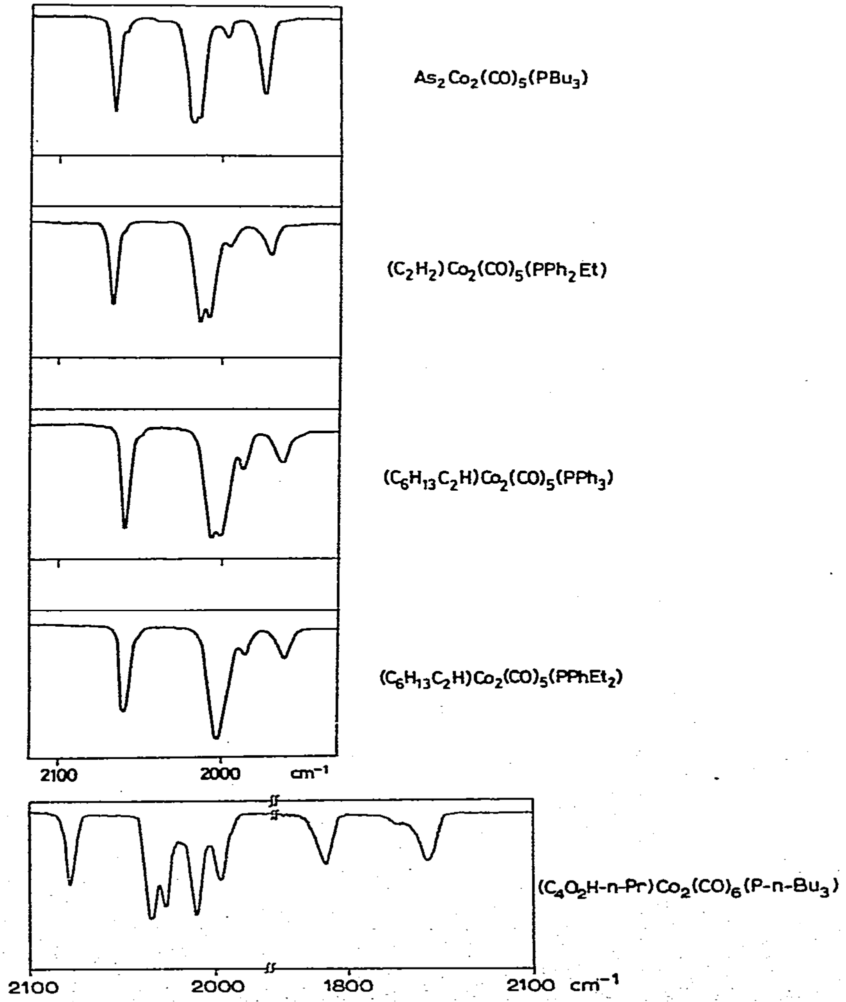

Fig. 1. ν(C—O) spectra of some $(\mu_2$-L$)(\mu_2$-L$')Co_2(CO)_5(PR_3)$ (with L = L$'$ and L ≠ L$'$) compounds and of $(C_4O_2H$-n-Pr$)Co_2(CO)_6(P$-n-$Bu_3)$.

that this degeneration was observed in cases where both the $R'C_2R''$ and PR_3 ligand are of strongly electron-donor character *.

A similar coincidence of the bands corresponding to the $\nu_2(a_1)$ and $\nu_6(b_2)$ vibrations ** of $(\mu_2\text{-}R'C_2R'')Co_2(CO)_6$ complexes was observed [9] in cases where both R' and R" were of strong electron-acceptor character (e.g. R' = R" = Cl, Br, I). Comparing these results it seems to be likely that these effects are due to a deformation of the molecular geometry caused by a marked deformation of the electron system of the molecule.

A comparison of spectra listed in Tables 1—3 shows that the position of the bands mirrors mainly the basicity of the phosphine, however it is also influenced by the nature of the bridging substituent (s).

The effect of the PR_3 and $P(OR)_3$ ligands can be seen quantitatively from the difference ($\Delta\bar{\nu} = \bar{\nu}_S - \bar{\nu}_P$) of the average ν(C—O) frequencies of the starting compounds ($\bar{\nu}_S$) and of the phosphine-substituted derivatives ($\bar{\nu}_P$).

The ν_S values could be calculated for the $(\mu_2\text{-}E_2)Co_2(CO)_6$ (E = P, As) compounds on the basis of measured [3] ν(C—O) data as well as of calculated [10] absorption maximum values of the IR-inactive $\nu_3(a_2)$ vibration. In the case of the acetylene complex $(\mu_2\text{-}R'C_2R'')Co_2(CO)_6$ (R' = R" = H, Ph; R' = H, R" = Ph) five experimental ν(C—O) frequencies [10,11] and a calculated [10] $\nu_3(a_2)$ value could be used to obtain $\bar{\nu}_S$. The average frequencies of the other acetylenic complexes were obtained using published [11] and measured (cf. Experimental) spectra as well as a $\nu_3(a_2)$ value of $\nu_5(b_1) - 4.2\ \text{cm}^{-1}$ which seems to be reasonable on the basis of a series of calculated [10] $\nu_3(a_2)$ values. Finally, $\bar{\nu}_S$ values for the $Co_2(CO)_7(C_4O_2R'R'')$ compounds were calculated solely on the basis of experimental [4a,11] data, all six terminal ν(C—O) fundamentals being IR active.

The title compounds may have 2 or 3 isomeric forms (Fig. 2) derived from an octahedral configuration of the Co atoms, which can be accepted on the basis of X-ray structures of $Co_2(CO)_8$ (bridged form) [12], $(PhC_2Ph)Co_2(CO)_6$ [13], $P_2Co_2(CO)_5(PPh_3)$ [14] and $As_2Co_2(CO)_5(PPh_3)$ [2]. As we have shown, each of the compounds investigated has only one isomeric form. We suggest this form to be of the axial substitutional type (forms A_1 and B_1 in Fig. 2) for the following reasons:

(i) The X-ray structures of two compounds $P_2Co_2(CO)_5(PPh_3)$ and $As_2Co_2(CO)_5(PPh_3)$ [2,14] show these to contain the phosphine ligand in the axial position.

(ii) The $\Delta\bar{\nu}$ values of the other PPh_3 derivatives are close to those of the compounds with known structures. Furthermore, the $\Delta\bar{\nu}$ shifts of the rest of the PR_3 and $P(OR)_3$ derivatives seem to be controlled primarily by the nature of the phosphine ligand. These facts suggest that all monosubstituted derivatives we have investigated have the same configuration, i.e. an axial type of substitution.

(iii) Among the substituents of the Co atoms the Co—Co bond can be supposed to be the least electron donor in character [15] since it is an electron-

---

* In other compounds I and II of similar character a rather low level of separation (cf. Table 1) of these two bands can be found.

** Assignment according to [10].

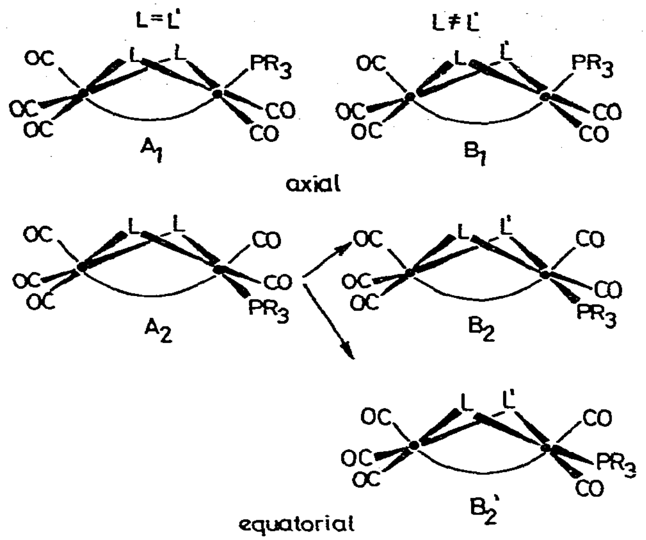

Fig. 2. Possible isomers of monosubstitution products of $(\mu_2\text{-L})(\mu_2\text{-L}')Co_2(CO)_6$ (with L = L' and L ≠ L') compounds.

compensation σ-bond and there is no reason to expect a partial charge transfer from one metal to the other in the unsubstituted products. It seems reasonable to suppose that the relatively strong electron donor PR_3 or $P(OR)_3$ ligands will therefore favour the position *trans* to the Co—Co bond [16,17]. This argument could perhaps be generalized for analogous compounds, as e.g. $(\mu_2\text{-SR})_2Fe_2(CO)_5(PR')_3$ [18].

(iv) The above picture is in good agreement with structural results obtained with the tetranuclear cobalt-carbonyl derivatives of phosphinoacetylenes: $(R_2PC_2R')_2Co_4(CO)_{10}$ [19]. In the case of these compounds two "$(R'C_2)Co_2(CO)_5(PR_2)$" units are bound together by means of dative bonds of the phosphorus atoms: the phosphorus on the acetylene ligand of one unit acts as donor substituent of the other and vice versa, but the position of both of the phosphorus atoms, (as donors) is axial, as is supposed in our case.

(v) The axial type of substitution can be expected on the basis of the often-forgotten principle of "minimum structural change" [20] since in this case at least one of the two σ_v planes of the starting compound (or at least of the $Co_2(CO_{term.})_6$ moiety) remains unaltered.

It should be noted here that recently several examples of equatorial substitution in compounds of similar structures could be found (e.g. derivatives of $Co_2(CO)_8$ (bridged) [21] or $(\mu_2\text{-RS})_2Fe_2(CO)_6$ [22]. However, equatorial substitution in these compounds is found always in disubstituted derivatives. In these cases the metal—metal bond and also the μ_2-ligand(s) may already conduct charge transfer to the "other" metal and thus the "second" donor substituent could also enter in the equatorial position. This effect, sometimes together with steric factors [21], may be strong enough to result in an equatorial position for both substituents, at least in the final structure of the models mentioned above.

The shift of the ν(C—O) band of the bridging carbonyl group in the lactone complexes III (relative to the unsubstituted compounds) is very near to the average values ($\bar{\nu}_p$) of the terminal carbonyls.

Phosphine substitution seems to have a moderate effect on the "organic" ν(C—O) vibrations of the lactone rings in compounds III. The extent of this effect could be evaluated only in two cases because of Fermi resonance splitting of the organic ν(C—O) band of the starting compounds in the others [4].

Experimental

Starting materials, $Co_2(CO)_8$ [23], $P_2Co_2(CO)_6$ [3], $As_2Co_2(CO)_6$ [2,3], acetylene-$Co_2(CO)_6$ compounds [6,24], the "lactone" complexes, $Co_2(CO)_7$-(C_4O_2RR') [4,5] as well as some of the ligands PPh_2Et [25], $PPhEt_2$ [25], $P(CH_2Ph)_3$ [26] and P(cyclo-C_6H_{11})$_3$ [27] were prepared by published procedures. Others were of commercial origin.

IR spectra were recorded by an UR-20 type instrument of Carl Zeiss Jena, using simultaneous DCl calibration according to [28]. Molecular weights were measured (in benzene) by a Knauer vapour phase osmometer.

Reaction of the cobalt carbonyls with the ligands were performed under rather similar conditions. One illustrative example is given below.

($C_6H_{13}C_2H$)$Co_2(CO)_5$P(cyclo-C_6H_{11})$_3$

79 mg (0.20 mmol) ($C_6H_{13}C_2H$)$Co_2(CO)_6$ (chromatographically pure) and 62 mg (0.22 mmol) P(cyclo-C_6H_{11})$_3$ were dissolved in 25 ml n-hexane. The solution was stirred at room temperature until vigorous CO evolution ceased (10 min), then at 60°C for 4 h. After having cooled to room temperature, the solution was evaporated to 5 ml.

This solution was eluted from silica gel by n-hexane. The first reddish-brown fraction was collected and concentrated in vacuo.

Then the solution was chilled to —78°C. The reddish-brown crystals were filtered and recrystallized twice from n-hexane. Yield 61 mg (47%). (Analysis Found: Co, 19.2; P, 5.1; mol. wt., 636. $C_{31}Co_2H_{47}O_5P$ calcd.: Co, 20.1; P, 4.8%; mol. wt., 648.)

In the course of this work 39 PR_3 and $P(OR)_3$ derivatives were prepared, 10 of which were characterized analytically *, the rest by analogy through their chromatographic and IR behaviour. The yields given in Tables 2 and 3 are rounded values obtained by measuring the weight of chromatographically pure products; yields of recrystallized products were generally lower by 5—10%.

The isomeric composition of 9 compounds was tested by repeated chromatography on a 150 × 1.5 cm silica gel column. The compounds were eluted by n-hexane (with the exception of the "lactone" derivative $Co_2(CO)_6$(P-n-Bu_3)-(C_4O_2HH) which was re-chromatographed with benzene). At least 3 cuts were taken from the band corresponding to the compound tested. High resolution IR spectra (in n-hexane) were taken from each cut. The IR ν(C—O) spectra of these cuts were found to be identical in all cases. These compounds included the 5 compounds with only 4 ν(C—O) fundamentals, (C_2H_2)$Co_2(CO)_5$(PR_3) (R =

---

* Co, P and mol. wt. values were satisfactory.

n-Bu and cyclo-C_6H_{11}), $(C_6H_{13}C_2H)Co_2(CO)_5P(OPh)_3$ and $Co_2(CO)_6(P\text{-}n\text{-}Bu_3)(C_4O_2HH)$.

Acknowledgement

The authors are indebted to Prof. L. Markó (Veszprém) for valuable advice. Sincere thanks are due to the Hungarian Oil and Gas Research Institute for help in the preparation of $Co_2(CO)_8$ as well as to Mr. I. Vecsei and Mr. I.T. Horváth for experimental assistance. One of the authors (G.V.) acknowledges a fellowship from the Hungarian Ministry of Education.

References

1 G. Váradi, A. Vizi-Orosz, S. Vastag, G. Pályi and L. Markó, (a) Xth Hung. Coll. Coordin. Chem., Györ, 26—28 May, 1975, (b) VIIIth Intern. Conf. Organometal. Chem., Venice, 1-5 September, 1975, Abstr. p. 31, 1975.
2 A.S. Foust, M.S. Foster and L.F. Dahl, J. Amer. Chem. Soc., 91 (1969) 5633.
3 A. Vizi-Orosz, G. Pályi and L. Markó, J. Organometal. Chem., 60 (1973) C25.
4 a. G. Pályi, G. Váradi, A. Vizi-Orosz and L. Markó, J. Organometal. Chem., 90 (1975) 85.
b. D.S. Guthrie, I.U. Khand, G.R. Knox, J. Kollmeier, P.L. Pauson and W.E. Watts, J. Organometal. Chem., 90 (1975) 93.
5 H.W. Sternberg, J.G. Shuykys, C. Belle Donne, R. Markby, R.A. Friedel and I. Wender, J. Amer. Chem. Soc., 81 (1959) 2239.
6 U. Krüerke and W. Hübel, Chem. Ber., 94 (1961) 2829.
7 R.F. Heck, J. Amer. Chem. Soc., 85 (1963) 657.
8 Y. Iwashita, F. Tamura and A. Nakamura, Inorg. Chem., 8 (1969) 1179.
9 G. Váradi, Thesis, University of Veszprém, 1972.
10 G. Bor, Symp. Metal Carbonyls, Ettal (Germany), 1974.; J. Organometal. Chem., 94 (1975) 181.
11 G. Bor, Chem. Ber., 96 (1963) 2644.
12 O.S. Mills and G. Robinson, Proc. Chem. Soc., (1959) 156; G.G. Summer, H. Klug and L.E. Alexander, Acta Cryst., 17 (1964) 732.
13 W.G. Sly, J. Amer. Chem. Soc., 81 (1959) 18.
14 L.F. Dahl and C.F. Campara, unpublished observations.
15 P.S. Braterman, Struct. Bonding, 10 (1972) 57.
16 A. Pidcock, R.E. Richards and L.M. Venanzi, J. Chem. Soc. A, (1966) 1707; L.M. Venanzi, Chem. Brit., (1968) 162; F.A. Cotton and C.S. Kraihanzel, J. Amer. Chem. Soc., 84 (1962) 4432.
17 T.G. Appleton, H.C. Clark and L.E. Manzer, Coordin. Chem. Rev., 10 (1973) 335.
18 L. Maresca, F. Greggio, G. Sbrignadello and G. Bor, Inorg. Chim. Acta, 5 (1971) 667.
19 N.K. Hota, H.A. Patel, A.J. Carty, M. Matthew and G.J. Palenik, J. Organometal. Chem., 32 (1972) C15, C35; H.A. Patel, A.J. Carty and N.K. Hota, J. Organometal. Chem., 50 (1973) 247.
20 J.A. Müller, Bull. Soc. Chim. France, 45 (1886) 438; J.A. Müller and E. Peytral, C.R. Acad. Sci. Paris, 179 (1924) 831; F.O. Rice and E. Teller, J. Chem. Phys., 6 (1938) 489; 7 (1939) 199; J. Hine, J. Amer. Chem. Soc., 88 (1966) 5525; J. Org. Chem., 31 (1966) 1236; S. Ehrenson, J. Amer. Chem. Soc., 96 (1974) 3778.
21 A.R. Manning, J. Chem. Soc., A, (1968) 1665; D.J. Thornhill and A.R. Manning, J. Chem. Soc. Dalton, (1973) 2086; (1974) 6.
22 J.A. De Beer and R.J. Haines, J. Organometal. Chem. 36 (1972) 297; 37 (1972) 173.
23 P. Szabó, L. Markó and G. Bor, Chem. Techn., 13 (1961) 549.
24 R.S. Dickson and P.J. Fraser, Advan. Organometal. Chem., 12 (1974) 323.
25 C. Stuebe, W.M. Le Suer and G.R. Norman, J. Amer. Chem. Soc., 77 (1955) 3526.
26 R.C. Hinton and F.G. Mann, J. Chem. Soc., (1959) 2835.
27 K. Issleib and A. Brack, Z. Anorg. Allg. Chem., 277 (1954) 266.
28 G. Bor, Acta Chim. Acad. Sci. Hung., 34 (1962) 315.

Note added in proof. After this manuscript had been mailed we became aquainted with the results of Manning and this coworkers (L.S. Chia, W.R. Cullen, M. Franklin and A.R. Manning, to be published). These authors prepared a series of mono- and di-substituted derivatives of $(RC{\equiv}CR')Co_2(CO)_6$ complexes with mono- and bi-dentate Group V ligands. Their results seem to be in good agreement with those in this paper.